

## Chapter 2

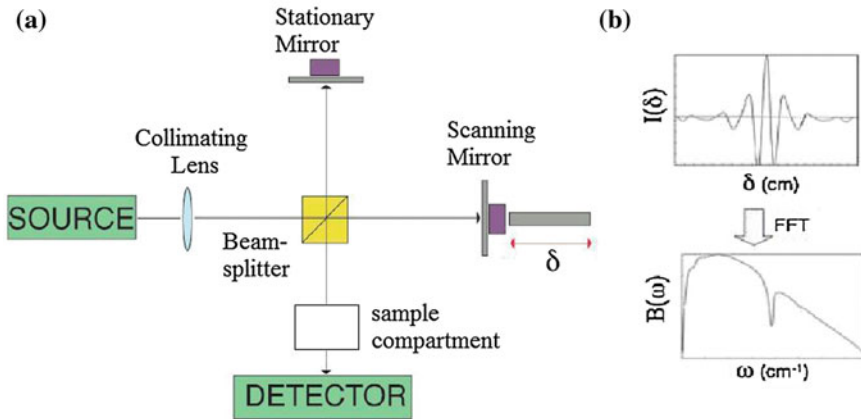
# Experimental Technique, Sample Fabrication and Models for Data Analysis

**Abstract** In this chapter the experimental technique used is described. The Fourier Transform Infrared Spectroscopy allows one to perform reflectivity and transmittance measurements as a function of frequency in a wide spectral range, from the far infrared to the ultraviolet. Through Kramers-Kronig transformations it is possible to calculate the linear optical response functions of the material. In this sections the experimental apparatus is also described and the models used to analyze both the reflectivity and transmittance data are discussed. The last part is dedicated to a brief description of the fabrication of plasmonic devices based on TI thin films and to the fitting of the data.

### 2.1 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) is a powerful technique to obtain a rapid and broad-range spectral analysis of the electromagnetic radiation, from the far infrared ( $\sim 1\text{meV}$ ) to the ultraviolet ( $\sim 5\text{eV}$ ) with high spectral resolution. The spectrometer used is a Michelson Interferometer, whose scheme is shown in Fig. 2.1. From a point source, using collimating mirrors, the electromagnetic radiation is sent to a beam-splitter (BS) that separates it into two components. Those components are sent one to a steady mirror and the other one to a scanning mirror. Thereafter the signals are recombined in the BS and focused on the detector. The intensity, which is detected as a function of the optical path difference  $\delta$  generated by the scanning of the moving mirror of the interferometer, is the interferogram  $I_R(\delta)$  and contains implicitly the whole frequency dependence of the light. The Fourier transform of  $I_R(\delta)$  permits to reconstruct the frequency spectrum of the light  $S(\omega)$  through the relation

$$B(\omega) \propto \int \left[ I_R(\delta) - \frac{1}{2} I_R(0) \right] \cos(2\pi\omega\delta) d\delta \quad (2.1)$$



**Fig. 2.1** Schematics of a Michelson Interferometer (a). The interferogram and the corresponding power spectrum obtained through a Fast Fourier Transform (FFT) procedure are shown (b)

where  $\omega$  is in  $\text{cm}^{-1}$  (wavenumbers). In the case of a monochromatic light source, the interferogram is a periodic sine function and the spectrum is a delta function centered at the frequency of the light. In the more realistic case of broadband light, the interferogram has an oscillating shape, sharply peaked at the zero-path-difference (ZPD) position and the related spectrum is a superposition of all the radiation frequencies, as can be seen in Fig. 2.1b.

The main advantages of the FT-IR Spectroscopy in respect to other techniques that use different spectrometer, like prisms or gratings, are:

- its wide spectral range of investigation is powerful for all the low-energy excitations in solid state physics.
- its very high resolving power, proportional to the length  $\delta$  of the arm of the scanning mirror.
- its optical precision in determining the optical path difference  $\delta$ : the position of the scanning mirror is indeed measured by means of a laser light (*Connes advantage*).
- its capability to measure simultaneously all the frequency spectrum, reducing the collecting time by a factor  $n$  (where  $n$  is the number of points in the spectrum) and improving the signal-to-noise ratio by a factor  $N^{1/2}$ , where  $N$  is the number of acquired and averaged spectra (*Fellgett advantage*).
- its use of a circular aperture that allows one to enhance the light intensity with respect to the case of linear slits (*Jacquinot advantage*).

A disadvantage of this technique is the need of Kramers-Kronig transformations (non local procedure) to extract both the real and imaginary parts of the response functions for bulk systems, requiring extrapolated reflectivity data from zero to the lowest measured frequency and from the highest measured to  $\infty$ . This can be avoided

by performing two independent measurements, as it is done in ellipsometry or in combined reflectivity and transmittance measurements, to obtain both the real and the imaginary part of the optical responses by a local procedure.

In the present work, FT-IR has been used to study the response of four bulk samples and two thin films of Topological Insulators. This can be done with FT-IR by sending the radiation modulated by the interferometer onto the sample and then measuring the intensity of either the reflected or transmitted radiation relative to a reference. The resulting reflectivity and the transmittance are

$$R(\omega) = \frac{I_r(\omega)}{I_0(\omega)} \quad (2.2)$$

$$T(\omega) = \frac{I_t(\omega)}{I_0(\omega)} \quad (2.3)$$

where  $I_0(\omega)$  is the intensity reflected by a reference mirror or that or transmitted by an aperture. Using our experimental setup, we were able to measure  $R(\omega)$  at near-normal incidence in a wide frequency range (from  $40\text{ cm}^{-1}$ , to  $22,500\text{ cm}^{-1}$ , i.e. from 5 meV to 2.8 eV) and  $T(\omega)$  at near-normal incidence in the far-infrared (from  $40\text{ cm}^{-1}$ , to  $400\text{ cm}^{-1}$ , i.e., from 5 meV to 50 meV) by varying the temperature of the sample from 10 K to 500 K. The frequency of the radiation will be hereafter expressed in  $\text{cm}^{-1}$  with an implicit factor  $2\pi c$ . An other disadvantage of the FT-IR technique is the lack of high-flux broadband conventional radiation sources. For that reason it is useful to use a source brilliant even at low frequencies, namely in the TeraHertz (THz) and sub-THz regions ( $1\text{ THz} \cong 33\text{ cm}^{-1}$ ), where the electrodynamics of the TI is concentrated.

### 2.1.1 Coherent Synchrotron Radiation at BESSY

Synchrotron Radiation (SR) is the radiation emitted by an accelerated charge at relativistic speed with typical energy of the order of a few GeV. SR is a very powerful source for investigations in the ultraviolet and X-ray spectral ranges. Infrared spectroscopy usually uses either black-body sources, or synchrotron radiation. Both these sources are incoherent if we consider the phase relationship in time and space between two different points of the wave front. Indeed, one has

- spatial coherence if two points belonging to a wave front have a fixed phase relation
- temporal coherence if two points along the wave propagation direction and belonging to two different wave fronts have a fixed phase relationship.

However, especially in the far infrared, infrared synchrotron radiation (IRSR) presents several advantages with respect to black bodies. IRSR is a continuous-wave incoherent radiation

- with a strong reduced thermal noise.
- with an intensity over small areas several order of magnitude bigger than those of conventional sources.
- with an emission strongly collimated.
- with a broad-band emission.
- with high degree of polarization.

In a storage ring or a synchrotron, bunches of electrons (or positrons) with mass  $m$  e charge  $q$ , initially accelerated by a linear accelerator (Linac), circulate along closed paths, recovering their energy when passing through a radiofrequency cavity with an electric field oscillating at MHz frequencies. In Fig. 2.2 it is shown how magnetic dipoles deflect the trajectory of the bunch with a curvature radius  $\rho$ . SR is emitted to the observer  $O$  along the tangent to the path and collimated within an angle  $1/\gamma$  (where  $\gamma = \frac{1}{\sqrt{1-\beta^2}}$  is the relativistic factor). In the infrared, the vertical divergence increases with the wavelength as  $\lambda^{1/3}$ .

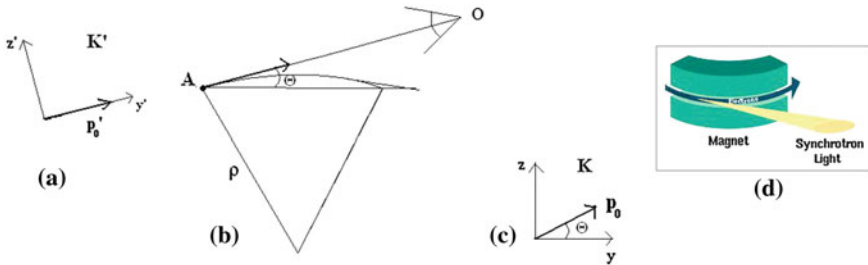
Short bunches come out from the radiofrequency cavity and move along the ring, emitting SR pulses in the undulators and in the bending magnets. Each bunch emits incoherent SR with a total intensity equal to the sum of the intensities emitted by all the electrons, irrespective of their relative phase. Hence, the total intensity is proportional to the number of particles and to the fourth power of their energy.

An impulse of duration  $\tau/2$  gives an intensity, obtained from the Fourier transform of the impulse, which is

$$I \propto \left( \frac{\sin(\omega\tau/2)}{\omega\tau/2} \right)^2 = \text{sinc}^2(\omega\tau/2). \quad (2.4)$$

It has a maximum frequency  $\omega_{max}$  due to relativistic effects and given by the equation

$$\omega_{max} \sim \frac{1}{\tau} \simeq 2 \frac{\gamma^3 c}{\rho}. \quad (2.5)$$



**Fig. 2.2** Scheme for emission of Synchrotron Radiation:  $O$  is the observer and  $\rho$  is the curvature radius (b);  $K$  and  $K'$  are the reference and laboratory system, respectively, where  $\mathbf{p}_0$  ( $\mathbf{p}_0'$ ) is the impulse of the bunch (a), (c). Sketch for collimated emitted radiation (d)

Below  $30\text{cm}^{-1}$  (about 1 THz) the brilliance can be widely increased by using Coherent SR (CSR).

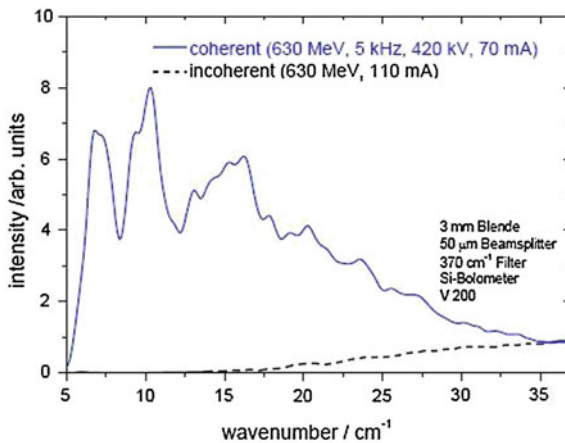
CSR is due to the interference between the electric fields of longitudinally-packed electrons. When the wavelength  $\lambda$  of emitted radiation is comparable with the length of the bunch, all the electrons emit radiation in phase and the irradiated power is proportional to the square of their number ( $N^2$ ). The emitted power,  $P$ , can be derived from the incoherent single-particle power,  $P_{1, \text{incoh}}$  [1], by the equation

$$P = N P_{1, \text{incoh}} (1 + N f_\lambda) \quad (2.6)$$

where  $f_\lambda$  is a form factor, derived from the Fourier transform of the longitudinal electron density in the bunch. For  $N f_\lambda \gg 1$  phase correlation is achieved and mostly coherent synchrotron radiation is emitted with power  $\propto N^2$ . In the case of a Gaussian bunch-density distribution the form factor is given by  $f_\lambda = \exp[-(2\pi\sigma/\lambda)^2]$ .

The emission of coherent radiation in the FIR (wavelength of few mm) can be obtained for a special magnetic optics operation in third-generation storage rings, which is called low- $\alpha$  mode. In standard synchrotron runs, coherence is suppressed by shielding effects of the dipole vacuum chamber [2, 3]. To overcome this limitation the bunch length and shape are manipulated by tuning the storage ring optics into a dedicated low- $\alpha$  mode, where  $\alpha$  is the momentum compaction factor, describing the orbit length variation with beam energy ( $\alpha = (\delta L/L)/(\delta p/p)$ ) [4, 5]. This yields shorter bunches and at higher beam currents of non-Gaussian shape, shifting the CSR spectrum with respect to the shielding cutoff. Above a certain threshold current, bunch instabilities are involved in the emission process, which leads to a periodic or even stochastic bursting [6]. These instabilities can limit the usability of the radiation for spectroscopic applications but enhance the emitted CSR power.

The above described operation mode is available twice a year at the Synchrotron Bessy II. Figure 2.3 shows a comparison between incoherent IRSR and CSR: the



**Fig. 2.3** Comparison between incoherent and coherent SR in the sub-THz region at Bessy II

latter one is clearly more intense than the former one in the sub-THz region, with a cut-off at the lowest frequency due to both to the efficiency of the optical components used in experiments and to the losses for diffraction along the optical path.

## 2.2 Experimental Apparatus

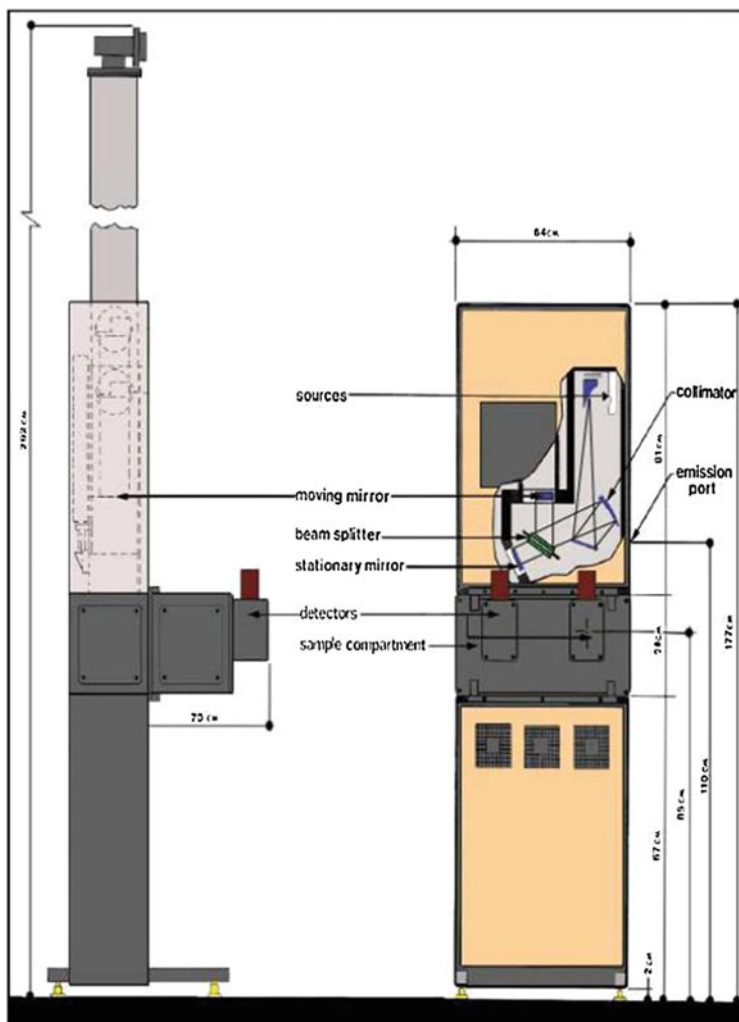
In this section we describe the two experimental apparatus that were used to perform temperature-dependent measurements. The BOMEM DA-3 Interferometer used to measure the reflectivity from mid-infrared to visible of the four TI crystals at IRS laboratory in Rome and the Bruker IFS 66v/S interferometer, used to measure the far-infrared and the sub-THz region of the same sample and the two TI thin films at the beamline IRIS at the Synchrotron BESSY in Berlin. The second apparatus is also the same used at IRS laboratory to measure the patterned TI films. In this section we describe the single parts coupled to the main compartment of the interferometers necessary to measure at low temperature and low frequencies.

### 2.2.1 BOMEM DA-3 Interferometer

BOMEM DA-3 is a vertical interferometer (see Fig. 2.4) whose main compartment allocates sources, beamsplitter and the optics. The moving (scanning) mirror moves within a vertical arm, returning to the initial position with a controlled *flyback*. A horizontal sample compartment is connected to the main compartment and both a close-cycle cryostat and a heating system are inserted into it. The different detectors can be mounted on the modular sample compartment. The two compartments can be evacuated independently to a minimum pressure of about 1 mbar. In Fig. 2.5 the sections (seen from the top) of these two parts are shown, together with the reflectivity setup.

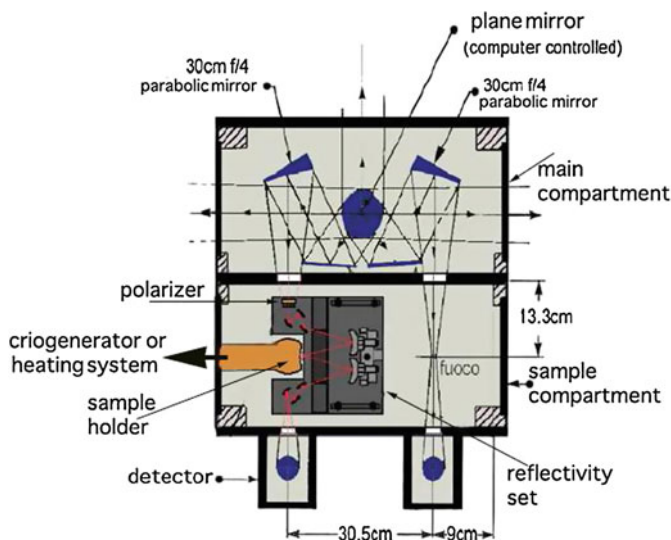
The reflectivity set up is made of a series of eight aluminum mirrors. The first one and last three mirrors are plane, while the central mirrors are spherical, in order to focus the beam onto the sample and then to refocalize the reflected light onto the detector (see the radiation path through the reflectivity setup indicated by a red line in Fig. 2.6). The central mirrors are moved by remotely controlled motors to allow in-vacuum alignment and easy recover of any misalignment due to mechanical stresses of the optical setup.

Conventional sources were provided by the interferometer manufacturer (BOMEM). The power supply was stabilized by standard electronics and a water cooling system was used for the sources, in order to obtain an emission of radiation as stable as possible [7, 8]. The beamsplitter, located in the main compartment of the interferometer, can be changed depending on the investigated spectral range. The standard commercial detectors employed are:

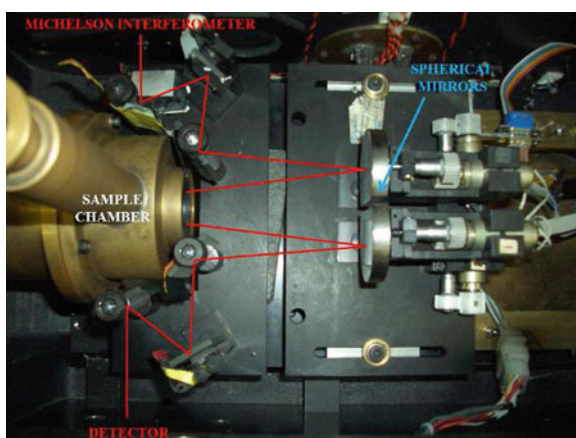


**Fig. 2.4** Scheme of BOMEM DA-3: side and front view. The location of sources and beamsplitter are shown, as well as the moving mirror

- *Ge InfraredLabs Bolometer* contained in a Dewar flask and provided of low-passing filters; it works at a temperature of 4.2 K and it is used for a frequency range below  $650\text{ cm}^{-1}$ ;
- a *photoconductive* nitrogen-cooled *HgCdTe* detector used from 500 to  $10,000\text{ cm}^{-1}$ ;
- a *Si photodiode* for frequencies higher than  $9,000\text{ cm}^{-1}$ .



**Fig. 2.5** Section of sample and main compartments of BOMEM DA-3. *Red lines* indicate the path of radiation within the reflectivity setup



**Fig. 2.6** Picture of the reflectivity setup in the sample compartment of BOMEM DA-3. The optical path from the main compartment to the detector is indicated by a *red line*

One can note that the detector ranges do not coincide neither with the frequency ranges of the sources nor with those of the beamsplitters. This means that many measuring sessions were required on the same sample. In Table 2.1, the minimum measuring sessions required to complete the full range, from the far infrared to the visible, for a given sample are listed [9].

**Table 2.1** Experimental setup for each of the infrared ranges investigated, defined by the intervals  $\omega_L \div \omega_H$ 

| Range   | $\omega_L \div \omega_H$<br>( $\text{cm}^{-1}$ ) | Source          | Beam<br>splitter                | Polarizer/<br>window | Detector<br>( $T$ ) |
|---------|--------------------------------------------------|-----------------|---------------------------------|----------------------|---------------------|
| far-IR  | 10–60                                            | Hg arc          | Mylar<br>50 $\mu\text{m}$       | Polyethylene         | Bolometer<br>1.6 K  |
|         | 20–100                                           | Hg arc          | Mylar<br>25 $\mu\text{m}$       | Polyethylene         | Bolometer<br>1.6 K  |
|         | 30–220                                           | Hg arc          | Mylar<br>12 $\mu\text{m}$       | Polyethylene         | Bolometer<br>4.2 K  |
|         | 190–660                                          | Globar          | Mylar<br>3 $\mu\text{m}$        | KRS5                 | Bolometer<br>4.2 K  |
|         | 30–660                                           | Hg arc          | Si-covered<br>My6 $\mu\text{m}$ | Polyethylene         | Bolometer<br>4.2 K  |
| mid-IR  | 500–6,000                                        | Globar          | Ge on<br>KBr                    | KRS5                 | HgCdTe<br>77 K      |
| near-IR | 4,000–12,000                                     | Quartz-<br>halo | Quartz                          | KRS5                 | HgCdTe<br>77 K      |
| Visible | 12,000                                           | Quartz          |                                 | Polaroid/            |                     |
|         | 24,000                                           | -halo           | Quartz                          | Quartz               | Si 295K             |

Note that many far-IR ranges overlap to get independent determination of the far-IR reflectivity

### 2.2.2 Closed-Cycle Cryostat

A closed-cycle cryostat Leybold COOLPACK 6000 (see Fig. 2.7) has been used in order to perform reflectivity measurements at low temperature. It is a cryogenerator based on a thermodynamic cycle (Gifford-Mac Mahon cycle) able to reach a minimum of 10 K on its cold finger, on the end of which the sample is mounted. A thermometer and a heating coil are mounted on the cold finger, allowing one for regulation of the temperature within 1 K. One can also strongly reduce thermal losses within the second stage screwing a thermal shield on the first stage, surrounding the second one.

The sample is glued by silver paint, to ensure thermal contact, on a brass cone, similar to those described by Homes et al. in Ref. [10]. The cone reflects the radiation that doesn't hit the sample in different directions with respect the normal reflection. The cone can also be aligned, using three tilting screws, to make the sample surface perpendicular to the incident radiation. The final alignment of the sample is made *in situ* using a laser beam or the inner visible source of the interferometer, directly, if the sample reflects well in the visible range.

Moreover, to avoid strong condensation of water, carbon dioxide or a thin solid nitrogen layer over the sample surface, the chamber of the cryostat is kept by two *turbomolecular* pumps at a pressure of about  $10^{-6}$  mbar. Often the cold finger itself it is used as a pump, after a first cooling cycle, allowing one to reach pressures of about  $10^{-7}$  mbar and allowing precise T-dependent measurements also at high frequency.



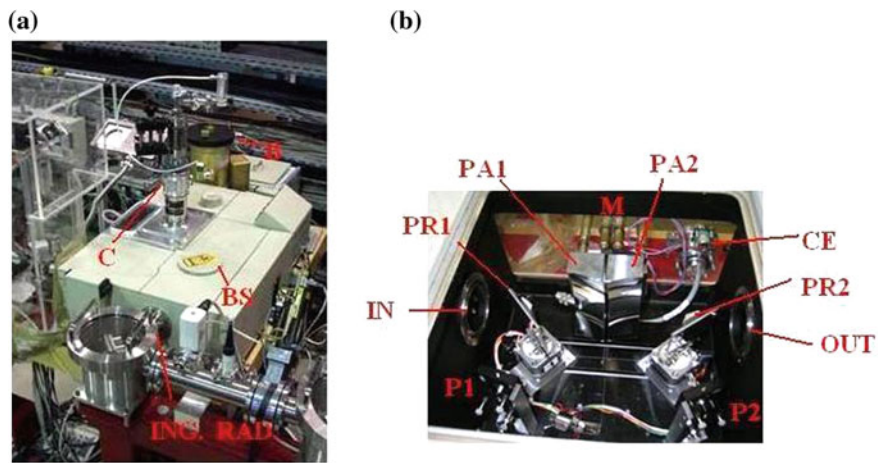
### 2.2.3 *Infrared Experimental Station at BESSY II: Bruker IFS 66v/S Interferometer*

We have measured the reflectivity and the transmittance at low temperature, down to 5 K, of our samples in the far-infrared and sub-THz regions at the beamline IRIS of the Synchrotron BESSY II at the Helmotz Zentrum in Berlin. A Bruker IFS 66v/S interferometer has been used, shown in a picture in Fig. 2.8a, e in its all parts in Fig. 2.9. It's a versatile instrument, whose components can be all remotely controlled *via* software, so that different measurement configuration can be set without any need to ventilate the interferometer. The alignment may also be made by using the remote control of any mirror by software. The interferometer is divided into several independent compartments, as shown in Fig. 2.9. The A compartment is the building block of the interferometer, composed by the radiation sources, the beam splitter, the fixed mirror and the mobile mirror capable of moving on an air-cushion; this limits the friction effect on the mirror movement but also can compromise the vacuum conditions in the compartment. In the B compartment finds place the setup for transmittance or reflectivity measurements. The C compartment contains all the internal detector and the E section contains the building block of the electronics of the instrument. As one can see in panel L, the radiation source is in one of the two focal points of an elliptical mirror. Light coming from the source is driven into the aperture wheels toward a parabolic mirror, which converts it in a plane wavefront. After passing through the beam splitter and covering the optical path in the two arms of the interferometer, it is focused by a second parabolic mirror in the sample compartment (see Fig. 2.8b) and then reaches the detector. The sample is mounted at the end of a vertical liquid-helium cryostat (see below). Some of the key features and performances of the Bruker IFS 66v/s interferometer can be summarized as follows:

- Full spectral range coverage from the Terahertz ( $< 5 \text{ cm}^{-1}$ ) up to the vacuum UV ( $\sim 30.000 \text{ cm}^{-1}$ ).
- Spectral resolving power of better than  $100.000 : 1$  or  $< 0.1 \text{ cm}^{-1}$  spectral resolution.
- Outstanding signal-to-noise: peak-to-peak noise of less than  $10^{-5}$  AU achieved within 1 min and  $4 \text{ cm}^{-1}$  spectral resolution.
- Time resolved spectroscopy: more than 100 spectra/sec Rapid Scan at  $12 \text{ cm}^{-1}$  spectral resolution; step scan temporal resolution of  $< 10 \text{ nsec}$  in the mid IR.
- slow Scan with less than  $0.006 \text{ cm/sec}$  optical velocity.

The different optical configurations used are listed in Table 2.2.

The optical and plasmonic responses of a patterned TI is strongly dependent on the polarization of the electromagnetic radiation. For this reason the measurements of the patterned with a grating TI thin film have been performed with polarized light. A polyethylene-based metallic wire polarizer from 10 to  $220 \text{ cm}^{-1}$  with an efficiency of 98 percent has been chosen for the far-infrared, THz and sub-THz regions, in order to match its range of efficiency with that one of any other window of the optical setup (see Table 2.2).



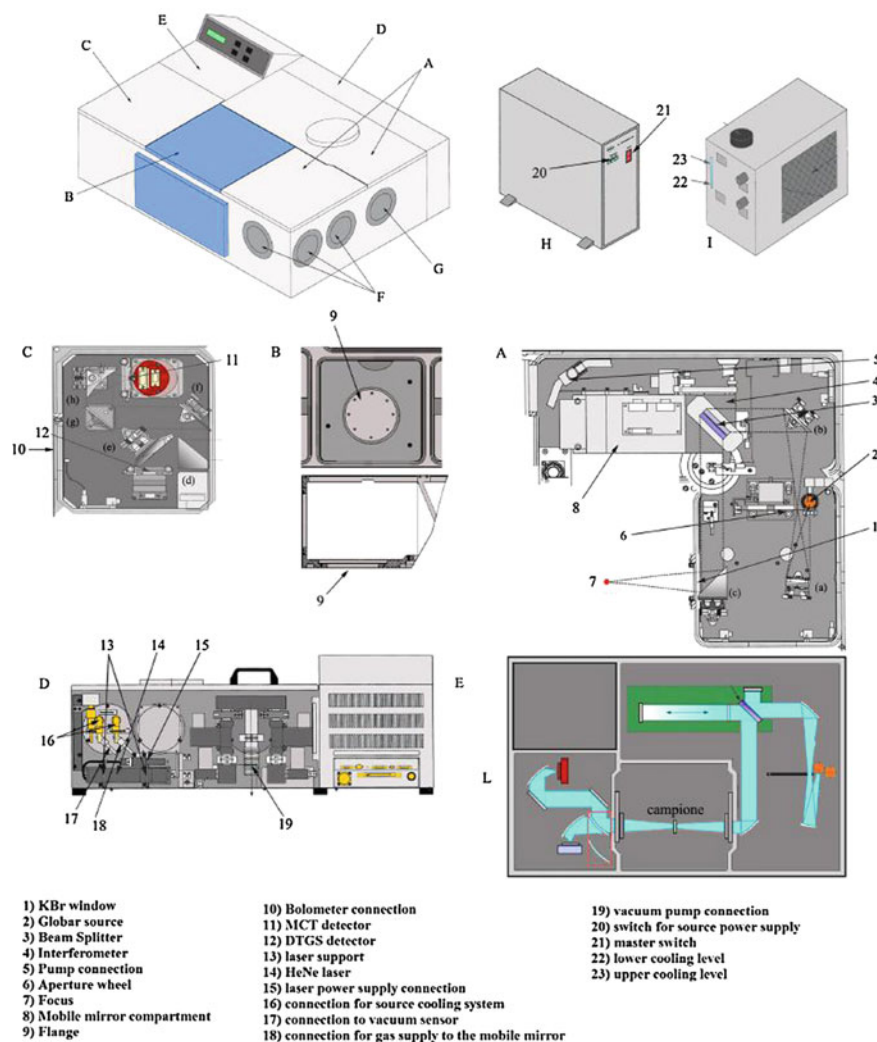
**Fig. 2.8** External view of the interferometer with the cryostat mounted on it at BESSY (a); reflectivity set inside the Bruker with four plane mirrors PR1, PR2, P1, P2 and two paraboloid mirrors PA1 and PA2. They collect the radiation from IN to the sample and then to the detector (OUT) (b)

**Table 2.2** Optical configurations used to cover the different spectral range with the Bruker interferometer at BESSY II

| Spectral range | Frequencies $\text{cm}^{-1}$ | Source     | Beamsplitter                                         | Optical window | Polarizer    | Detector        |
|----------------|------------------------------|------------|------------------------------------------------------|----------------|--------------|-----------------|
| FIR            | 50–600                       | Globar, Hg | Ge-covered Mylar $6\text{ }\mu\text{m}$              | Polyethylene   | Polyethylene | Bolometer 4.2 K |
| THz            | 10–100                       | Hg         | Mylar $25\text{--}50\text{--}125\text{ }\mu\text{m}$ | Picarin        | Polyethylene | Bolometer 4.2 K |
| Sub-THz        | 5–10                         | SR         | Mylar $50\text{ }\mu\text{m}$                        | Picarin        | Polyethylene | Bolometer 1.6 K |

### 2.2.4 Liquid-Helium Cryostat and Pumped Bolometer

We used a vertical continuous-flow liquid helium cryostat (*Janis model*) in order to measure low temperature reflectivity and transmittance. It is able to reach a minimum  $T = 5\text{ K}$  on its coldfinger, at the end of which there is the sample holder, as shown in Fig. 2.10. A thermometer and a heating coil are mounted on the top and around the coldfinger, respectively, in order to ensure an external temperature control within  $\pm 0.5\text{ K}$ . A thermal shield is screwed on the lower part of the first stage, allowing one to reduce the radiation heating from the surrounding second stage. The vertical under vacuum movement of the sample holder is allowed by a mechanic external stage, which provides micrometric displacements. For transmittance measurements we can mount on the sample holder both the sample and the bare substrate, as reference,



**Fig. 2.9** An overall sketch of the Bruker IFS 66v/S interferometer and details of the different components. **A** Michelson's interferometer compartment where a, b, c, d, e, f, g, h indicate the mirror succession, **B** sample compartment, **C** detector compartment, **L** optical scheme of the measurements with the interferometer

in order to measure them at the same time. The samples were mounted by means of brass plates fixed with brass screws, in order to maximize the thermal contact.

In the sub-THz region, using both an inner Hg lamp and the Synchrotron Radiation as a source, we have been used a Ge Bolometer as a detector, which, in particular conditions, can measure down to  $4\text{ cm}^{-1}$ . The bolometer is a thermal detector, used in the FIR, made of a doped semiconductor (Ge) which, when hit by electromagnetic



**Fig. 2.10** A picture of the liquid helium cryostat sample holder with (*right panel*) and without (*left panel*) the thermal screen. The arrow indicates the position where the sample is placed during the measurements

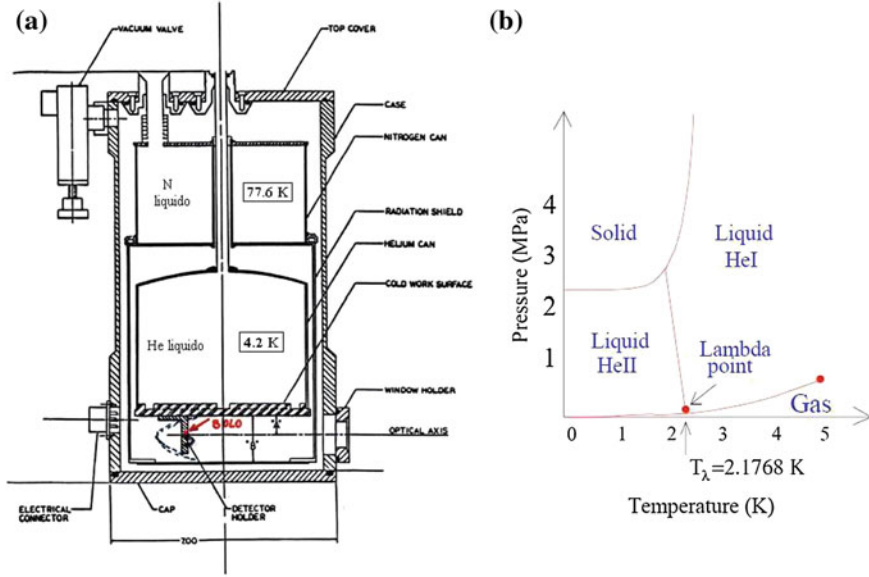
radiation, changes its resistivity with the variation of temperature. The semiconductor is in thermal contact with a chamber filled with liquid helium, so its starting working temperature is 4.2 K (see the sketch in Fig. 2.11a) When FIR radiation hits the semiconductor its resistivity decreases: this variation can be measured as the variation of the potential difference, while a constant current flows through the bolometer. This gives information about the intensity of the radiation collected on the detector. The bolometer can measure down to  $15\text{--}20\text{ cm}^{-1}$  (depending on the signal-to-noise ratio due to the quality of the sample): this limit is given by the brilliance of the Hg lamp. Then, with CSR is necessary to use the bolometer in a different working point. This can be done pumping on the helium bath above the liquid inside the chamber: by decreasing the pressure down to 11 mbar, the liquid helium reaches the  $\lambda$ -point (see the phase diagram in Fig. 2.11b), becoming superfluid. Therefore, the semiconductor reaches  $T = 1.6\text{ K}$  and the detector can measure down to very low frequencies ( $\sim 4\text{--}8\text{ cm}^{-1}$ , depending on the signal-to-noise ratio and also on the size of the sample, which may give rise to diffraction processes with the large wavelengths of the electromagnetic radiation of this spectral range).

### 2.3 Reflectivity Measurements

The reflectivity measured in this work, at near-normal incidence for frequencies between  $30 \div 20,000\text{ cm}^{-1}$ , is defined as the ratio between the electromagnetic intensity reflected from the sample ( $I_r$ ) and that reflected from a reference mirror ( $I_0$ ) (see Eq. 2.2).

$R(\omega)$  is related to the complex refractive index  $\tilde{n} = n + ik$  via the Fresnel equations [11, 12]:

$$R(\omega) = |\tilde{r}|^2 = \left| \frac{\tilde{n} - n_W}{\tilde{n} + n_W} \right|^2 \quad (2.7)$$



**Fig. 2.11** Sketch of the inside part of a bolometer (a). Phase diagram of helium near the  $\lambda$  point (b)

where  $r$  is the reflection coefficient and  $n_W$  is the refractive index of the medium that shares the front interface with the sample. Whether the reflectivity is measured at a vacuum-sample interface  $n_W = 1$  and Eq. 2.7 reduces to the simple formula:

$$R(\omega) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}. \quad (2.8)$$

Since

$$r(\omega) = \ln \sqrt{R(\omega)} + i\theta(\omega) \quad (2.9)$$

where  $r(\omega)$  is the complex reflectance,  $R(\omega)$  e  $\theta(\omega)$  are related by the Kramers-Kronig (KK) transformations, that generally correlate the real and the imaginary part of a linear response function, due to the causality principle (see below).

### 2.3.1 Measuring the Reference: the Overfilling Technique

In order to obtain the absolute value of the reflectivity (Eq. 2.2), usually both the intensity reflected by the sample and the one reflected from a pre-aligned reference (a mirror) are measured at very temperature.

If, however, the sample is a small and irregular single crystal, diffraction becomes important, because it may arise from the imperfections and roughness, when the surface defect dimension is comparable with the average wavelength of the incident radiation. For commercial mirrors the roughness is typically smaller than the wavelength, therefore different diffraction effects could occur between the reflection by the sample and that one by the reference. Those diffraction effects can be accounted and partially eliminated with the overfilling technique: the sample surface itself is used as the reference, covering it by a gold (or silver) film, through in-vacuum metal evaporation. The thickness of such film is smaller than the surface defects dimension, then the diffraction effects become negligible (see Ref. [10]).

In Fig. 2.12 the evaporator scheme is shown. A short wire of the metal to be evaporated is threaded in a tungsten filament. The filament is connected to a wand, that can be raised or lowered from outside the cryostat, to be placed in front of the sample. The filament is usually in position 1, where it allows the passage of the light beam. When the spectra on the sample have been acquired at all temperatures, the sample is re-heated to room temperature; the filament is displaced to position 2, a current of about 3 A is applied, so that the metal melts and a film is deposited on the sample surface. The filament is then moved back to position 1 and the reference spectra are collected at all temperatures. It is common experience that the best deposition occurs when the sample is at room temperature.

It is worth noting that no optical path is changed during the deposition and that the interferometer is kept evacuated and free of any mechanical stress. Moreover, the overfilling technique allows one to recover the same thermal contractions both on the pure sample and on the metallic deposited foil, performing two different thermal cycles to acquire the spectra.

### 2.3.2 Kramers-Kronig Transformations

It is possible to derive the complex refractive index at every frequency by exploiting the Fresnel relation, equivalent to Eq. 2.7:

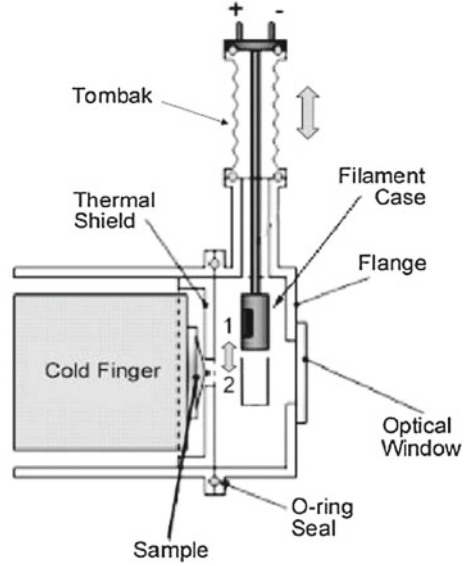
$$\tilde{r} = \frac{(\tilde{n} - 1)}{(\tilde{n} + 1)} \quad (2.10)$$

If one now uses the Maxwell equations for the electromagnetic field in matter to combine the real and the imaginary part of  $\tilde{n} = n + ik = \sqrt{\tilde{\epsilon}}$  [11], one obtains the components of the complex dielectric function  $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ :

$$\epsilon_1(\omega) = n(\omega)^2 - k(\omega)^2 \quad (2.11)$$

$$\epsilon_2(\omega) = 2n(\omega)k(\omega) \quad (2.12)$$

**Fig. 2.12** Scheme of the evaporator



Then, using the relation  $\tilde{\epsilon} = \epsilon_{\infty} + 4\pi\tilde{\sigma}/\omega$ , where  $\epsilon_{\infty}$  is the high-frequency dielectric constant, one can derive the complex conductivity  $\tilde{\sigma} = \sigma_1 + i\sigma_2$ :

$$\sigma_1(\omega) = \frac{\omega}{4\pi} \epsilon_2(\omega) \quad (2.13)$$

$$\sigma_2(\omega) = \frac{\omega}{4\pi} [\epsilon_{\infty} - \epsilon_1(\omega)] \quad (2.14)$$

Therefore, one can obtain all the microscopic response function of the system from the only knowledge of the frequency dependent complex reflectance  $\tilde{r}(\omega)$ . Its imaginary part can be, in fact, evaluated by extrapolating the experimental  $R(\omega)$  to  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  (the free electron asymptotic behavior  $R(\omega) \propto \omega^{-4}$  is generally used) and then performing the KK analysis.

KK transformations were introduced by Kramers [13–15] and Kronig [16, 17] in 1926 and still play a fundamental role in condensed matter. These relations can be derived from general considerations involving causality [11, 12] and have a wide application as they allow for the evaluation of the components of the complex dielectric function or the complex conductivity when only one quantity, such as the reflectivity or the absorbed power, is measured.

In the case of  $\tilde{r}(\omega)$ , the KK relation

$$\theta(\omega) = -\frac{2\omega}{\pi} P \int_0^{+\infty} \frac{\ln \sqrt{R(\omega')}}{(\omega')^2 - \omega^2} d\omega' \quad (2.15)$$

where  $P$  indicates the principal value of the integral. Similar KK relations can be written for the other optical functions, that is

$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^{+\infty} \frac{\omega' \epsilon_2(\omega')}{(\omega')^2 - \omega^2} d\omega' \quad (2.16)$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^{+\infty} \frac{[\epsilon_1(\omega') - 1]}{(\omega')^2 - \omega^2} d\omega' \quad (2.17)$$

$$\sigma_1(\omega) = \frac{2}{\pi} P \int_0^{+\infty} \frac{\omega' \sigma_2(\omega')}{(\omega')^2 - \omega^2} d\omega' \quad (2.18)$$

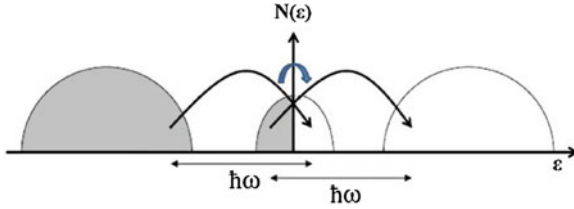
$$\sigma_2(\omega) = -\frac{2\omega}{\pi} P \int_0^{+\infty} \frac{[\sigma_1(\omega') - 1]}{(\omega')^2 - \omega^2} d\omega' \quad (2.19)$$

All the analysis performed in this work start from the complex conductivity and, in particular, from its real part  $\sigma_1(\omega)$  (called *the optical conductivity*). Therefore we give a more detailed description of its properties in the next Section.

### 2.3.3 Optical Conductivity and Sum Rules

The optical conductivity is defined as the linear response function relating the electrical current  $\mathbf{J}$  and the excitation due to an electric field  $\mathbf{E}$  by the expression  $\mathbf{J}(\mathbf{q}, \omega) = \tilde{\sigma}(\omega, \mathbf{q})\mathbf{E}(\mathbf{q}, \omega)$ . It is worth noting that in an optical experiment only the transverse conductivity is detected (i.e.  $(\mathbf{J} \perp \mathbf{q})$ ) due to the transverse properties of the oscillating electrical field, and that excitation of any energy can be detected but only at  $|\mathbf{q}| \sim 0$ . This latter condition is easily understood considering that, in order to conserve energy and momentum in an absorption process,  $\mathbf{q} = \frac{v}{c}\mathbf{k}$  is required, where  $v = v\mathbf{k}$  is the dispersion relation for the excitation. In condensed matter, no velocity  $v$  higher than  $10^6$  cm/sec (Fermi velocity in metals) is reached, while  $c \simeq 3 \cdot 10^{10}$  cm/sec, which implies  $|\mathbf{q}| \sim 0$  for any value of  $\omega$  in the optical range. As it was shown in the previous section, it is possible to obtain, from the measured  $R(\omega)$ , the frequency dependent conductivity  $\tilde{\sigma}(\omega)$ . We can derive an expression that relates the optical conductivity to microscopic observables that can be easily defined in a N-electron system. The fluctuation-dissipation theorem relates the fluctuations described by a correlation function to the dissipation described by the imaginary part of a susceptibility. In the case of response to the electromagnetic radiation, the interaction Hamiltonian, in the dipole approximation, reads  $H_{int} = -\frac{1}{c}\mathbf{J} \cdot \mathbf{A}$ , where  $\mathbf{A}$  is the perturbing vector potential. The following expression of the fluctuation-dissipation theorem can be derived directly from the Fermi golden rule

$$\sigma_1(\omega) = \sum_n \frac{1}{\hbar\omega V} \int_0^\infty dt \langle n | \{\hat{\mathbf{J}}(0), \hat{\mathbf{J}}(t)\} | n \rangle e^{i\omega t}, \quad (2.20)$$



**Fig. 2.13** Sketch of a density of states (grey: occupied, white: unoccupied). The optical conductivity at a given frequency  $\omega$  is the sum of all the transitions from an occupied to an empty state separated by an energy  $\hbar\omega$

which is called the Kubo formula [12].

The right hand side of Eq. 2.20 can be independently derived from the Fermi golden rule for the transition probability between two energy levels, once summed over all the possible initial and final states. This allows one to establish a proportionality relation between  $\sigma_1$  and the total transition rate  $W$ , from which one gets a microscopic interpretation of the conductivity, as the sum over all the possible “jumps” of energy  $\omega$  in a given distribution of states  $\varepsilon_n$ , weighted by their dipole matrix element, and whose ground state energy is  $\varepsilon_g$  (Fig. 2.13):

$$\sigma_1(\omega) = \frac{\pi}{V} \sum_n |\langle n | \hat{\mathbf{J}} | g \rangle|^2 \frac{\delta(\omega - \varepsilon_n + \varepsilon_g)}{\varepsilon_n - \varepsilon_g} \quad (2.21)$$

It can be shown [12] that, by combining Kramers-Kronig relations with physical arguments about the behavior of the real and imaginary part of the response function it is possible to establish a set of so-called sum rules for various optical parameters. We will here define only the *conductivity sum rule* as:

$$\frac{\omega_p^2}{8} = \int_0^\infty \sigma_1(\omega, T) d\omega = \frac{\pi N e^2}{2m} = \frac{\pi}{2} \sum_j \frac{q_j^2}{M_j} \quad (2.22)$$

where  $\omega_p$  is the plasma frequency (defined as  $\omega_p = \left(\frac{4\pi N e^2}{m}\right)^{1/2}$ ). The charge and the mass of the  $j$  charged objects in the solid unit cell have been generalized to  $q$  and  $M$ , respectively, to include the case of phononic excitations. It is worth noting that  $N$  is, for more than one electron per atom, the total number of electrons per unit volume if the integral (2.22) is carried out to infinite frequencies. This means that, at high enough frequencies, also the core electrons are excited. The sum rule evaluated up to high frequency expresses a constraint that  $\sigma_1$  must fulfill when some external parameters vary, such as the temperature  $T$  or the pressure  $P$ . Once chosen a cutoff frequency  $\Omega$  to evaluate the integral in Eq. 2.22, the spectral weight is defined by

$$W(\Omega, T) = \int_0^\Omega \sigma_1(\omega, T) d\omega. \quad (2.23)$$

In a conventional material  $W$  has a cutoff at  $\omega_p$ , the plasma edge, which separates low-energy (intraband) from high-energy (interband) charge excitations. The spectral weight is conserved at  $\omega_p$ .

## 2.4 Transmittance Measurements

In this work the transmittance of four TI thin films has been measured, both in the case of bare films on  $\text{Al}_2\text{O}_3$  substrate and in that of patterned films (with a grating of different widths).

As we have already seen, the transmittance in the absence of interference effects, here neglected due to the sample roughness, is given by the Eq. 2.3 or, equivalently, by

$$T(\omega) = \frac{[1 - R(\omega)]^2 e^{-\alpha(\omega)t}}{1 - R(\omega)^2 e^{-2\alpha(\omega)t}} \quad (2.24)$$

where  $R(\omega)$  is the reflectivity,  $\alpha(\omega)$  is the absorption coefficient and  $t$  is the thickness of the sample. Otherwise, the transmittance of a film deposited on a substrate, measured relative to the transmittance of the substrate itself, is related to real and imaginary parts of the sheet conductance  $\tilde{\sigma}_\square(\omega)$  of the film [18], by

$$T(\omega) = \frac{1}{\{1 + Z_0 \sigma'_\square(\omega)/[\tilde{n}(\omega) + 1]\}^2 + \{Z_0 \sigma''_\square(\omega)/[\tilde{n}(\omega) + 1]\}^2} \quad (2.25)$$

Here  $Z_0 = \sqrt{\mu_0/\epsilon_0} = 377\Omega$  is the impedance of free space,  $\tilde{n}(\omega)$  is the complex refractive index of the substrate, and  $\sigma'_\square(\omega)$  and  $\sigma''_\square(\omega)$  are the real part and the imaginary part of the sheet conductance of the film, respectively, where

$$\tilde{\sigma}_\square(\omega) = \tilde{\sigma}(\omega)t \quad (2.26)$$

with  $\tilde{\sigma}(\omega)$  the complex conductivity of the film.

### 2.4.1 Local Procedure for the Extraction of the Conductance

From Eq. 2.25 it is possible to extract directly the real part of the conductance, from which one can derive, by 2.26, the optical conductivity of the material. Hence, inverting the 2.25, we have

$$\sigma'_{\square}(\omega) = \frac{[\tilde{n}(\omega) + 1]}{Z_0} \left( \frac{1}{T(\omega)} - 1 \right) - \sigma''_{\square}(\omega) \quad (2.27)$$

One can calculate the imaginary part of the conductance, fitting the transmittance by the Eq. 2.25, in which one can extract both the real and the imaginary part of the conductance by means of the Drude-Lorentz model (see Sect. 2.6.1).

Actually, in most experiments  $\sigma''_{\square}(\omega) \ll [\tilde{n}(\omega) + 1]/Z_0$ . In this case the contribution of the imaginary part of the conductance to the transmittance is negligible and one can approximate the (2.27) as

$$\sigma'_{\square}(\omega) \simeq \frac{[\tilde{n}(\omega) + 1]}{Z_0} \left( \frac{1}{T(\omega)} - 1 \right) \quad (2.28)$$

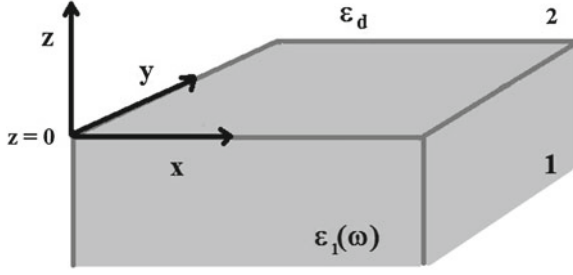
Furthermore, if the complex refractive index of the substrate  $\tilde{n}(\omega) = n(\omega) + ik(\omega)$  has the real part  $n$  more or less constant as a function of frequency and  $k \ll n$ , then one can approximate again the (2.28) as

$$\sigma'_{\square}(\omega) \simeq \frac{[n + 1]}{Z_0} \left( \frac{1}{T(\omega)} - 1 \right) \quad (2.29)$$

### 2.4.2 Surface Plasmon Polariton

When an electric field hits a metal, free electrons are displaced from their position. The resulting lack of negative charge gives rise to a Coulombian attraction, which forces them to their original position. This produces an oscillating charge density called *plasmon*, with a characteristic resonance frequency (*plasma resonance*) given by  $\omega_p = \sqrt{ne^2/\epsilon_0 m}$ , where  $n$  is the free-carrier density,  $e$  and  $m$  the electronic charge and mass, respectively, and  $\epsilon_0$  the vacuum dielectric constant. One usually refers to this collective mode as *bulk plasmon*. If the charge oscillation is confined at the interface between the metal and a dielectric medium, the relative activated collective mode is called *Surface Plasmon Polariton* (SPPs). Here the term *polariton* is referred to the hybrid nature of collective modes at low wave vectors, when they strongly interact with light [19].

The electromagnetic behavior and the dispersion relation of SPPs can be derived from Maxwell's equations with appropriate boundary conditions in a simple geometric model shown in Fig. 2.14, with the plane  $z = 0$  as the interface between the metal and the dielectric medium. The first medium (medium 1,  $z < 0$ ) has permittivity  $\epsilon_1(\omega)$  ( $\epsilon_2(\omega) = 0$  because no damping is considered), while the second one (medium 2,  $z > 0$ ) has positive permittivity  $\epsilon_d$ . The direction of propagation of the surface mode is assumed along  $x$ , so that the electric field can be written  $\mathbf{E}(x, y, z) = \mathbf{E}(z)e^{i\beta x}$ , where  $\beta = k_x$  is the propagation constant, which corresponds to the component of the wave vector of light along the direction of propagation of the traveling wave.



**Fig. 2.14** Geometric model for the interface configuration between two media, sustaining SPPs

Now, considering a Helmholtz equation where the field has the above form, one can obtain the wave equation for a surface wave, namely

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + (k_0^2 \epsilon - \beta^2) \mathbf{E} = 0 \quad (2.30)$$

where  $\epsilon$  is  $\epsilon_1$  or  $\epsilon_d$  for the medium 1 or 2, respectively. If one now uses the Maxwell's equations assuming harmonic time dependence ( $\frac{\partial}{\partial t} = 0$ ), one-dimensional geometry and a uniform field in the plane ( $\frac{\partial}{\partial y} = 0$ ), one has:

$$\frac{\partial E_y}{\partial z} = -i\omega\mu_0 H_x \quad (2.31)$$

$$\frac{\partial E_x}{\partial z} - i\beta E_z = -i\omega\mu_0 H_y \quad (2.32)$$

$$i\beta E_y = i\omega\mu_0 H_z \quad (2.33)$$

$$\frac{\partial H_y}{\partial z} = -i\omega\epsilon_0 \epsilon E_x \quad (2.34)$$

$$\frac{\partial H_x}{\partial z} - i\beta H_z = -i\omega\epsilon_0 \epsilon E_y \quad (2.35)$$

$$i\beta H_y = -i\omega\epsilon_0 \epsilon E_z \quad (2.36)$$

Such system of equations allows for two solutions with different polarization properties: TM (Transverse Magnetic) and TE (Transverse Electric). For the former mode only the components  $E_x$ ,  $E_z$  and  $H_y$  are non zero (electric field parallel to the  $xz$  plane), while for the latter one only  $H_x$ ,  $H_z$  and  $E_y$  are non zero (electric field parallel to the  $xy$  plane).

Let us first consider the TM modes. By applying Eqs. 2.37 to the non zero components in both semispaces one obtains:

$$H_y(z) = A_2 e^{i\beta x} e^{-k_2 z} \quad (2.37)$$

$$H_y(z) = A_1 e^{i\beta x} e^{-k_1 z} \quad (2.38)$$

$$E_x(z) = i A_2 \frac{1}{\omega \epsilon_0 \epsilon_2} k_2 e^{i\beta x} e^{k_2 z} \quad (2.39)$$

$$E_x(z) = -i A_1 \frac{1}{\omega \epsilon_0 \epsilon_2} k_1 e^{i\beta x} e^{k_1 z} \quad (2.40)$$

$$E_z(z) = -A_1 \frac{\beta}{\omega \epsilon_0 \epsilon_2} e^{i\beta x} e^{-k_2 z} \quad (2.41)$$

$$E_z(z) = -A_1 \frac{\beta}{\omega \epsilon_0 \epsilon_1} e^{i\beta x} e^{k_1 z} \quad (2.42)$$

where  $k_i = k_{z,i}$  ( $i = 1, 2$ ) is the component of the wave vector perpendicular to the interface in mediums 1 and 2, respectively. The reciprocal value of  $k_i$  defines the decay length of the evanescent fields perpendicular to the interface. The requirement of continuity for the electric field at the interface implies

$$A_1 = A_2 \quad (2.43)$$

$$k_2/k_1 = \epsilon_d/\epsilon_1 \quad (2.44)$$

Equation 2.44 subsists only if the two permittivities are of opposite sign, that is, the confinement implies that surface waves exist only between materials with the real parts of the permittivity of opposite sign. For the magnetic field the continuity brings to

$$k_1^2 = \beta^2 - k_0^2 \epsilon_1 \quad (2.45)$$

$$k_2^2 = \beta^2 - k_0^2 \epsilon_d \quad (2.46)$$

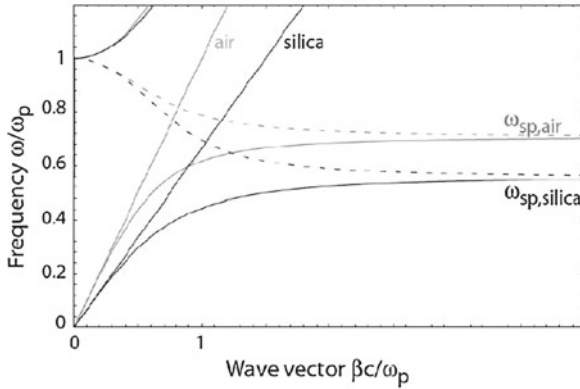
Now, combining Eqs. 2.44 and 2.45 one obtains the dispersion relation of the SPPs propagating at a single interface between a metal and a dielectric, i.e.:

$$\beta = k_{SPP} = k_0 \sqrt{\frac{\epsilon_1 \epsilon_d}{\epsilon_1 + \epsilon_d}} \quad (2.47)$$

where  $\beta$  is real, if no damping factor in the metal electric permittivity has been taken into account.

Considering now the TE mode and repeating the same procedure for the extraction of  $\beta$ , one finds for the continuity of the field that  $A_1 = A_2 = 0$ , so all the components of the fields are zero: this means that a SPP can exist only as TM mode.

In Fig. 2.15 the dispersion relations of a SPP on a metal/air and metal/silica interface are reported: in that plot SPPs correspond to the part of the dispersion curve on the right side of the corresponding light line of air or silica, due to the bound nature of the SPPs modes. On the contrary, radiative modes, coupled to light, lie at



**Fig. 2.15** SPP dispersion relations at an interface between metal/air and metal/silica. Both the wave vector and the frequency on the two axis are renormalized with respect to the plasma frequency. Solid curves refer to modes with real propagation constant  $\beta$ , dashed curved refer to non propagating modes (purely imaginary  $\beta$ )

frequencies  $\omega > \omega_p$ ; between the radiative regime and the bound one there is a band gap with purely imaginary wave vectors, where no propagating waves are allowed. In the low-frequency region (wave vectors in the mid-IR range and lower)  $k_{SPP}$  is close to the light dispersion line and the SPPs acquire the nature of grazing-incidence light field (the so called Sommerfeld-Zenneck waves [20]). For higher frequencies (larger wave vectors), on the contrary, SPPs approach the surface plasmon frequency  $\omega_{SP} = \omega_p / \sqrt{1 + \epsilon_d}$ : the group velocity of the excited mode goes to zero and the wave (also called *surface plasmon*) acquires an electrostatic character.

As we have assumed so far, no damping has been considered. The metal is treated as an ideal conductor, that is with the imaginary part of the electric permittivity equal to zero. Actually, excitations of the conduction electrons in a metal undergo damping: this leads to a complex electric permittivity and, hence, to a complex propagation constant  $\beta$ . Then, a damped SPP has a finite energy attenuation length  $L$ , called propagation length, given by:

$$L = \frac{1}{2\text{Im}[\tilde{\beta}]} \quad (2.48)$$

where  $\tilde{\beta}$  is the complex propagation constant given by Eq. 2.15 in the case of non zero imaginary part of the electric permittivity of the metal. Typical values of the propagation length are in the range  $10 \div 100 \mu\text{m}$ .

In contrast with the undamped SPP, the damped bound SPP approaches at high wave vectors a maximum finite wave vector in correspondence of  $\omega_{SP}$ : this fact provides a constraint on the minimum wavelength allowed for propagating SPPs, equal to  $\lambda_{SP} = 2\pi / \text{Re}[\tilde{\beta}]$ . Moreover this limits also the strength of the field confinement in the direction perpendicular to the interface: the field along  $z$ , in fact, decays as  $e^{-|k_z||z|}$  with  $\tilde{k}_z = \sqrt{\tilde{\beta}^2 - \epsilon_d (\frac{\omega}{c})^2}$ .

## Radiation Coupling to a Grating

In the previous Section we have seen that the SPPs dispersion relation lies below the light line: it means that no wave vector matching is possible between a SPP and a photon in that configuration. However, it is possible to excite a SPP introducing a coupling between it and light, just perturbing the periodicity along the metallic surface with a period multiple of the electromagnetic half-wavelength.

One can consider a system with the same periodicity along  $x$  and  $y$  as shown in Fig. 2.16a. For the wave equation solution a deformation of the surface like that acts as a spatially periodic perturbation with a certain period  $a$ , equal to the distance between two following defects (holes or other features). That structure produces a series of reflection planes for the electromagnetic wave, which will be diffracted according to the Bragg condition  $n\lambda = 2a$ , with  $n$  an integer and  $\lambda$  the SPP wavelength. Hence, the periodicity defines a Brillouin zone in the reciprocal lattice along  $k_x$ . That mechanism is analogous to the formation of gaps at the Brillouin zone boundary in the quasi-free electron model in crystalline solids and can be easily extended along the other directions when considering a 3D problem.

Therefore, the reciprocal lattice is able to provide the wave vector necessary to excite SPPs through an electromagnetic wave. The resulting conservation of the wave vector is:

$$\mathbf{k}_{SPP} = \mathbf{k}_x \pm i\mathbf{G}_x \pm j\mathbf{G}_y \quad (2.49)$$

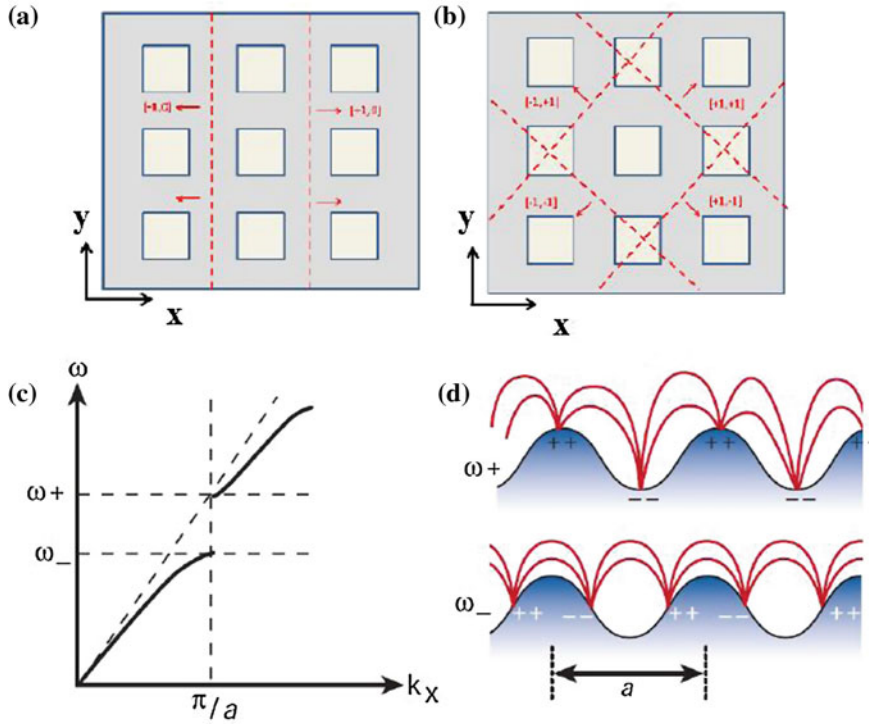
where  $i, j$  are integer (indicating the order of the scattering that couples the incident wave and the SPP),  $\mathbf{k}_x = \mathbf{k}_0 \sin\theta$  is the component of the light wave vector parallel to the interface along  $x$  and  $|\mathbf{G}_x| = 2\pi/a_x$  and  $|\mathbf{G}_y| = 2\pi/a_y$  are the reciprocal lattice vectors associated with the two periodicities of the perturbation. For a square array  $a_x = a_y = a$ , hence  $|\mathbf{G}_x| = |\mathbf{G}_y| = 2\pi/a$ . From Eqs. 2.49 and 2.47, one can obtain the dependence of the SPPs frequency on the in-plane wave vector on the periodic structure, that is

$$\omega = \left( \frac{\epsilon_1 + \epsilon_d}{\epsilon_1 \epsilon_d} \right)^{1/2} \sqrt{k_x^2 \pm 2i \left( \frac{2\pi}{a} \right) k_x + (i^2 + j^2) \left( \frac{2\pi}{a} \right)^2} \quad (2.50)$$

which can be written at normal incidence as:

$$\omega = \left( \frac{2\pi}{a} \right) \left( \frac{\epsilon_1 + \epsilon_d}{\epsilon_1 \epsilon_d} \right)^{1/2} \sqrt{i^2 + j^2} \quad (2.51)$$

It is worth noting that, when comparing Eqs. 2.49 and 2.47, it has been used an approximation, since the SPP dispersion, appropriate for a smooth film, neglects the fact that the periodic pattern may cause both a significant change in the dispersion and a large coupling between the front and the back surface of the metal film. In fact, as one can see in Fig. 2.16, Eq. 2.47 predicts the position of the plasmonic resonances of the unfolded SPP dispersion and a gap is opened at the edge of the Brillouin zone,

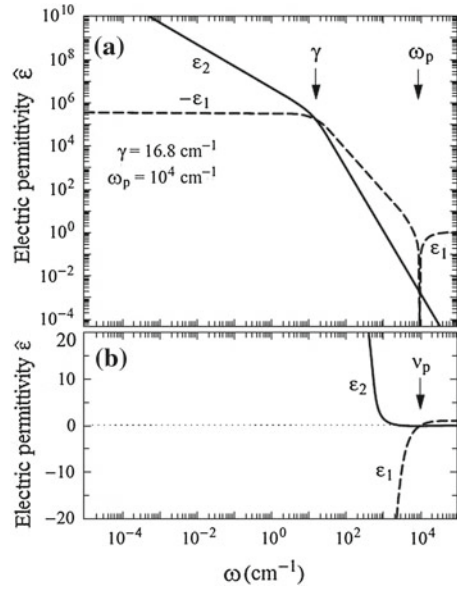


**Fig. 2.16** Scheme of the lowest order scattering of SPP excited on a periodic hole array which corresponds to the orders  $(\pm 1, 0)$  (a) and  $(\pm 1, \pm 1)$  (b). The arrows indicate the SPPs propagation direction. Periodic pattern of the metallic interface opens a band gap at a SPP wavelength equal to twice the period at the edges of the Brillouin zone (c). This leads to the formation of two standing wave solutions due to the different field and surface charge distribution (d) [21]

so that no propagating modes are possible at the frequency predicted by the smooth film equation. Actually, at the band edge the dispersion bands are flat. Therefore the group velocity of the SPP is equal to zero and the SPP density is extremely high. It means that at those frequencies one can find several SPP modes associated with different wave vectors, but to the same energy. Hence, a strong field rises in proximity of the metal surface at those frequencies. The strong enhancement of the electromagnetic field is one of the most important phenomena associated with SPPs.

Such process of localization and consequent enhancement of the field is due to a large propagation constant ( $\beta \gg nk_0$ , where  $n$  is the refractive index of the dielectric at the interface), therefore the exponential decay of the field results in its strong confinement at the interface. The upper limit for  $\beta$  in real metals (with electron damping) is fixed at the wave vector value corresponding to the surface plasma frequency. Due to their high free electron density ( $\sim 10^{23} \text{ cm}^{-3}$ ), most of common metals have their plasma frequency in the visible or ultraviolet frequency range. Therefore, in metals SPPs are strongly confined at the interface for visible

**Fig. 2.17** Real and imaginary part of the electric permittivity of a metal with  $\omega_p \sim 3 \times 10^{14} \text{ s}^{-1}$  and  $\gamma \sim 0.5 \times 10^{12} \text{ s}^{-1}$  in logarithmic (a) and linear (b) scale [12]



frequencies or higher: the so called *plasmonic regime* is established in that range. The requirement on the electric permittivity of the metal for a strong plasmonic regime is that the ratio of its real part over its imaginary part is much larger than unity, *i.e.*  $|\epsilon_1|/\epsilon_2 \gg 1$ . In Fig. 2.17 an example of the real and imaginary parts of the electric permittivity of a metal with  $\omega_p \sim 3 \times 10^{14} \text{ s}^{-1}$  ( $10^4 \text{ cm}^{-1}$ ) and damping  $\gamma \sim 0.5 \times 10^{12} \text{ s}^{-1}$  ( $16 \text{ cm}^{-1}$ ) is reported. For frequencies up to  $\gamma$  the absolute value of the real part of the electric constant is smaller than its imaginary part: this fact results in a non plasmonic regime ( $|\epsilon_1|/\epsilon_2 \ll 1$ ); on the contrary, above the frequency corresponding to the damping and below the plasma frequency the plasmonic regime is totally achieved.

If the frequency decreases from the visible range down to the THz range, the plasmonic regime weakens. In fact, the absolute value of the real and imaginary parts of the electric permittivity of metals are of the order of about  $10^5$ . This leads to a negligible penetration of the electric field inside the metal, hence to a strong delocalization [19, 22].

Some works showed that at 1 THz the electric field extends up to several centimeters above the metallic interface sustaining SPPs. According to their delocalized nature, SPPs in the THz range behave like a homogeneous field incident under a grazing angle on the metal interface, so they are often called Sommerfeld-Zenneck waves, as already mentioned above [23]. In the limit of Perfect Electric Conductor (PEC) (infinite real part of the electric permittivity), the electric field inside the conductor is equal to zero since no penetration is allowed: this means that a PEC can not support electromagnetic surface modes, like SPPs. However it has been demonstrated in Ref. [24] that a PEC film can sustain bound surface modes, which mimic

SPPs if a periodic perturbation is introduced. The periodic structure, in fact, allows the penetration of an average electric field and restores the conditions required for the existence of a *spoof* SPP, which dominates over the Sommerfeld-Zenneck waves given by the unpatterned conductor.

An expedient to increase the confinement of the SPPs in the THz range is the employment of poor metals or semiconductors, even highly doped: the capability to tune their carrier density, that is the plasma frequency of SPPs, by means of thermal control, photocarrier generation or direct carrier injection makes these materials good candidates for optoelectronic devices.

## 2.5 Sample Preparation

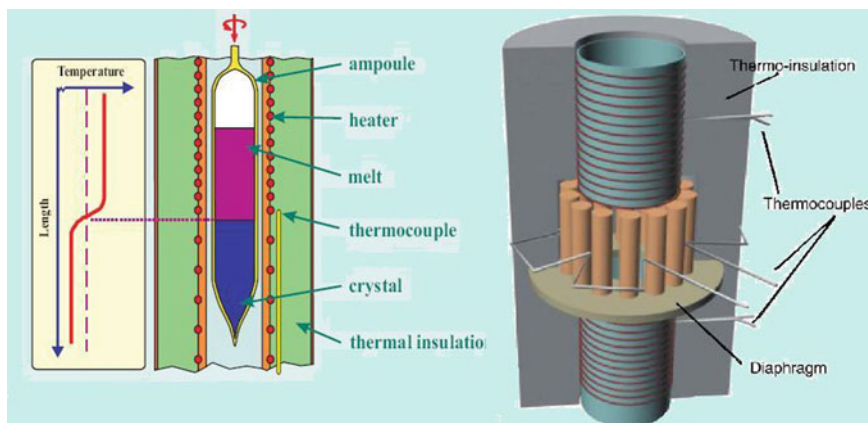
In this section we will briefly describe how the crystals and the films of topological insulators (TIs), measured for this work, have been grown. Two different techniques have been used by two experimental groups: the modified Bridgman method for the crystals growth by the Prof. R. J. Cava's group at the Department of Chemistry of the Princeton University (USA) and the Molecular Beam Epitaxy (MBE) for the films deposition by the Prof. S. Oh's group at the Department of Physics and Astronomy of Rutgers, the State University of New Jersey (USA).

### 2.5.1 Crystal Growth

Four Topological Insulator single crystals have been measured in this work:  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_{2-x}\text{Ca}_x\text{Se}_3$  with  $x=0.0002$ ,  $\text{Bi}_2\text{Se}_2\text{Te}$  and  $\text{Bi}_2\text{Te}_2\text{Se}$ . They were all grown in the Solid State Chemistry Research Group of Prof. Robert J. Cava at the Princeton University by the modified Bridgman and Bridgman-Stockbarger crystal-growth techniques.

The single crystal of  $\text{Bi}_{2-x}\text{Ca}_x\text{Se}_3$  was grown by the “modified Bridgman” method, that is via a process of two-step melting, starting with mixtures of high-purity elements (Bi, 99.999 %; Se 99.999 %; Ca 99.8 %). First, stoichiometric mixtures of Bi and Se were melted in evacuated ampoules at 800 °C for 16 h. Then, the melts were mixed before leading them to solidify by air quenching to room temperature. Second, the stoichiometric amount of Ca was added in the form of pieces, avoiding its contact with the quartz of the ampoule. Therefore, the materials were heated in evacuated quartz ampoules at 400 °C for 16 h and at 800 °C for a day. The crystal growth occurred by cooling from 800 to 550 °C over a period of 24 h, following an annealing at 550 °C for 3 days. Finally, the crystals were furnace cooled to room temperature, ready to be easily cleaved along the basal plane and cut into approximately  $1 \times 1 \times 6 \text{ mm}^3$  rectangular bar samples [25].

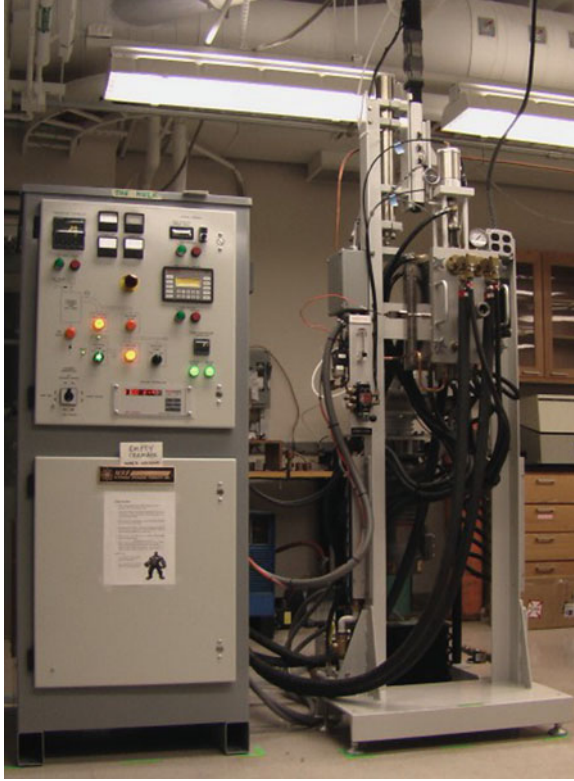
As expected for small-band-gap semiconductors, the quality of the crystals  $\text{Bi}_2\text{Se}_2\text{Te}$  and  $\text{Bi}_2\text{Te}_2\text{Se}$  from the perspective of the defects and the resultant carrier concentrations is strongly affected by small inhomogeneities in the chemi-



**Fig. 2.18** Cross section of the Bridgman-Stockbarger apparatus for the crystal growth (a) and three-dimensional view (b)

cal composition that occur during the crystal growth. In order to overcome that difficulty, a Bridgman-Stockbarger method was employed to fine-tune the chemical composition of the crystals and optimize the carrier concentration. Actually, single crystals of  $\text{Bi}_2\text{Te}_2\text{Se}$  were prepared by two methods: the “modified Bridgman” method and the classical Bridgman-Stockbarger method, whose apparatus is shown in Fig. 2.18. Using the first technique, five-gram mixtures of high purity elemental Bi, Te and Se were sealed in quartz ampoules and then heated up to  $850^\circ\text{C}$  for 1–2 days, followed by cooling to  $500^\circ\text{C}$  at  $6\text{--}12^\circ\text{C/h}$ . The samples were then annealed at  $500^\circ\text{C}$  for 3–4 days. The crystals obtained are within a large monolithic piece ( $\sim 1 \times 1 \times 4 \text{ cm}^3$ ), that usually consists of approximately ten grains presenting random crystal orientations. For the powder XRD (X-Ray Diffraction) characterization of the laboratory-made  $\text{Bi}_2\text{Te}_2\text{Se}$ , the samples from the “modified Bridgman” method were in addition annealed at  $400^\circ\text{C}$  for over 2 weeks and then quenched in cold water [26].

Samples of the related compound  $\text{Bi}_2\text{Se}_2\text{Te}$  were similarly prepared in accordance to the similar structure. The second method was also employed for those crystals, allowing for a fine-tuning of the chemical compensation near the stoichiometry composition, being natural variations in it along the directionally solidified crystal boule. Thirty grams of mixture was sealed in a long internally carbon-coated quartz ampoule (20 cm long and 0.8 cm of diameter). This ampoule was tapered at the bottom in order to favor seed selection, and then placed in a vertical furnace (see the picture in Fig. 2.19). The temperature profile of the furnace was set to ensure that the zone hotter than the melting temperature of the  $\text{Bi}_2\text{Te}_2\text{Se}$  was longer than the length of the liquid. The temperature gradient at the furnace position crossing the melting point of the  $\text{Bi}_2\text{Te}_2\text{Se}$  was  $\sim 30^\circ\text{C/cm}$ . The ampoule was then lowered through the hot zone at the speed of  $2\text{--}4 \text{ mm/h}$ . The crystal boules obtained were about 14 cm long with fewer than 10 crystals, which were all grown with their *ab* planes parallel



**Fig. 2.19** Vacuum Furnace (minimum pressure  $10^{-9}$  Torr, maximum temperature  $1,800^{\circ}\text{C}$ ) for the crystal growth at the Princeton University

to the long axis of the ampoule. The obtained uniform crystal morphology indicates that the boule is relatively homogeneous on a large scale, because its chemical composition gradually varies along the long axis during the directional solidification. The boule was finally cut to seven pieces of about 2 cm equal length, ready for transport measurements.

### 2.5.2 *Film Deposition*

The films of topological insulator  $\text{Bi}_2\text{Se}_3$  of two different thicknesses, here measured, were grown at the Rutgers University by a Molecular Beam Epitaxy (MBE) technique on 0.5 mm thick sapphire substrates  $\text{Al}_2\text{O}_3$  [27]. A custom-designed SVTA MOS-V-2 MBE system, whose base pressure was lower than  $5 \times 10^{-10}$  Torr, was used. Bi and Se fluxes were provided from Knudsen cells: the fluxes were measured using a quartz crystal microbalance Inficon BDS-250, XTC/3.

In order to start with a clean substrate surface,  $\text{Al}_2\text{O}_3$  (001) has been exposed to an ex situ UV ozone cleaning step before mounting it in the growth chamber to burn off most organic compounds that may be present on the surface. Then, to remove any further eventual contaminants from the substrate surface, the sapphire was heated to  $700^\circ\text{C}$  in oxygen pressure of  $10^{-6}$  Torr for 10 min. In order to monitor the cleaning and the growth of the samples, the substrate was observed with RHEED (Reflection High-Energy Electron Diffraction) before and after the treatment, by which a bright specular spot and Kikuchi lines were observed after heating and then cooling the substrate [28]: Fig. 2.21a, b indicates that this procedure improved the surface conditions. Therefore, using the two-temperature growth process,  $\text{Bi}_2\text{Se}_3$  films of various thickness were grown: their surface evolution during the growth was monitored by RHEED, as shown in Fig. 2.21c–f. After deposition of 3 quintuple layers (QLs) (1 QL<sup>1</sup> is about 1 nm) of  $\text{Bi}_2\text{Se}_3$  at  $110^\circ\text{C}$ , a sharp streaky pattern was observed, providing evidence for a single-crystal  $\text{Bi}_2\text{Se}_3$  structure. Then the film was slowly annealed to a temperature of  $220^\circ\text{C}$ , in order to further help the crystallization of the film, as one could see by the brightening of the specular spot. The diffraction pattern and the Kikuchi lines became increasingly sharp upon further  $\text{Bi}_2\text{Se}_3$  deposition: this marks that the grown films have atomically flat morphology and high crystallinity [28]. The film quality was further improved by annealing the sample at  $220^\circ\text{C}$  for an hour after the growth, leading to high quality single crystalline films with large planes and minimal bulk conduction [28].

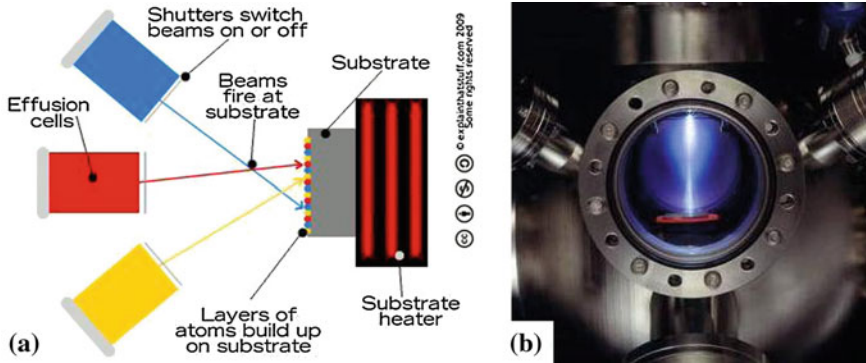
In Fig. 2.20a a sketch of the MBE apparatus is shown. Relatively precise beams of molecules (heated up so they're in gas form) are shot at the substrate from “guns” called effusion cells. One needs one “gun” for each different beam, shooting a different kind of molecule at the substrate, depending on the nature of the crystal. The molecules land on the surface of the substrate, condense, and build up very slowly and systematically in ultra-thin layers, so the complex, single crystal grows one atomic layer at a time. Separate beams fire different molecules and they build up on the surface of the substrate, arranging epitaxially on top of it. Figure 2.20b shows the nutshell of the MBE apparatus.

### 2.5.3 Patterning the Thin Films for Plasmonic Studies

The fabrication of the patterned TI thin films by a grating was performed in collaboration with the Institute for Photonics and Nanotechnology (IFN) in Rome. The IFN facility has a class 100–1000 Clean Room, that is an environment with a low level of pollutants (hundreds of particles/cubic feet having a  $0.5\ \mu\text{m}$  dimension). The Clean Room, 300 square meters wide, is equipped with several devices for film deposition,

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<sup>1</sup> TIs have a layered structure with five atomic layers as a basic unit, named a quintuple layer (QL), and the crystal structure is formed by the relatively strong covalent bond within a QL and the weak van der Waals interaction between QLs.



**Fig. 2.20** **a** Sketch of Molecular beam epitaxy (MBE) apparatus, creating a single crystal by building up orderly layers of molecules on top of a substrate (base layer). **b** Molecular beam epitaxy (MBE) in action. MBE takes place in ultrahigh vacuum chambers like this, at temperatures of around 500 °C, to ensure a totally clean, dust-free environment; the slightest contamination might damage the crystal. Photo by Jim Yost, courtesy of US DOE/NREL (U.S. Department of Energy/National Renewable Energy Laboratory)

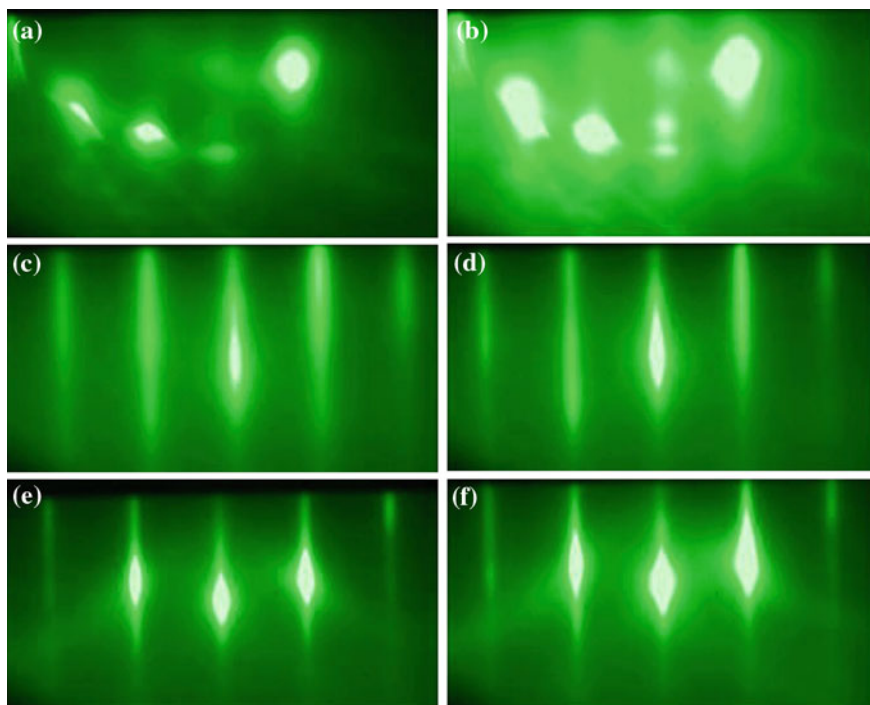
electronic and optical lithography, etching processes and diagnostic. In the following two sections we will shortly describe the fabrication technique of our optical devices.

### 2.5.4 Electron Beam Lithography

The fabrication of optical devices from Topological Insulator thin films, with thickness of about one hundred of nanometers, requires techniques capable of structuring material on a fine scale. Depending on the shape of the pattern to be fabricated, different resolutions are required, and therefore different techniques must be considered.

The most used fabrication technique for industrial application is Optical Lithography. It consists in the transfer of a pattern to a photosensitive material by selective exposure to a radiation source such as light. A photosensitive material is a material that experiences a change in its physical properties when exposed to a radiation source. If the exposure is selective, that is by masking some of the radiation with a resist film, a pattern on the material exposed is transferred, providing a difference between the properties of the exposed and unexposed regions. It is worth noting that the resolution of this technique is limited by the wavelength of the light source used to expose the resist.

For scientific application a higher resolution for the optical devices is given by the Electron Beam Lithography (EBL). EBL is a process similar to the Optical Lithography, except for using an electron beam instead of light for the exposure. This technique was first introduced in the sixties of last century using Electron Scan



**Fig. 2.21** RHEED (Reflection High-Energy Electron Diffraction) images showing the steps of  $\text{Bi}_2\text{Se}_3$  growth on sapphire substrates. Sapphire substrate mounted in the UHV growth chamber after UV-cleaned for 5 min (a). On heating to  $700^\circ\text{C}$  in an  $\text{O}_2$  pressure of  $1 \times 10^{-6}$  Torr for 10 min (b). After deposition of 3 QL of  $\text{Bi}_2\text{Se}_3$  film at  $110^\circ\text{C}$  (c). Specular beam spot gets brighter on annealing the film to  $220^\circ\text{C}$  (d). RHEED pattern gets much brighter and sharper on subsequent growth of another 29 QL at  $220^\circ\text{C}$  (e). Final RHEED pattern of the 32 QL film after being annealed at  $220^\circ\text{C}$  for an hour (f) [28]

Microscopes (SEM). Its key advantage consists in the possibility to overcome the limit of light diffraction, allowing for nanometric devices fabrication. Moreover the exposure can be done in batch processing. The main disadvantage is the long time that the exposure takes.

The EBL machine has an electron gun able to generate an electron beam with tunable current. The gun is made of a thermoionic emission cathode and uses some electrostatic and magnetic lenses to focus the electron beam up to a spot size of 2–4 nm on the sample. Usually the electron beam is sent on a substrate covered with an electronic resist and is deflected in order to write directly the pattern on the substrate. It has been used the EBL machine *Leica Microsystem EBPG 5000* at IFN for the fabrication of our samples.

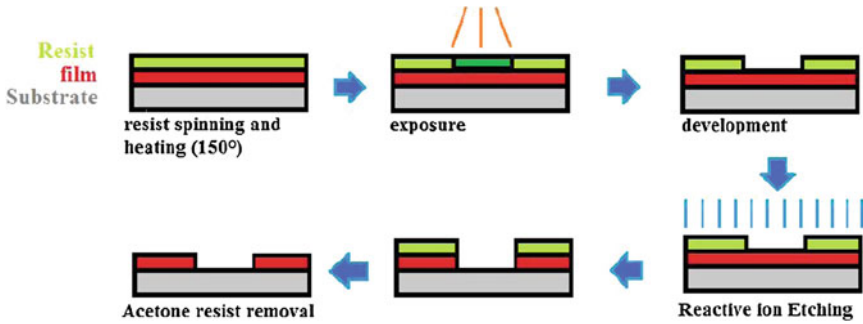


Fig. 2.22 Steps of the Etching procedure

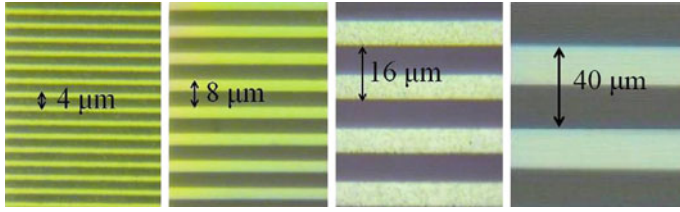
### 2.5.5 Reactive Ion Etching

After the lithography procedure, one can use two fabrication processes: the additive one, called *lift-off*, that adds the layer to be patterned on a bare substrate, a process very common for metallic films; the second one, that we have used, is the *etching*, common for semiconductors. The *etching* is a subtractive procedure which starts from the film deposited on a substrate, and patterns it by means of a chemical agent.

The basic steps for the *process*, shown in a sketch in Fig. 2.22, are:

- **Cleaning:** the sample is initially heated to a temperature sufficient to drive off any moisture that may be present on the surface.
- **Coating:** the sample is covered with photoresist by *spin coating*: a viscous, liquid solution of photoresist is spread over the sample surface and it is spun rapidly to produce a uniformly thick layer.
- **Baking:** the photoresist-coated sample is pre-baked, typically at 90–100°C for 30–60 s on a hotplate, to drive off the excess photoresist solvent.
- **Exposure:** the EBL process writes the desired pattern on the sample. When exposed, positive photoresist becomes soluble in the basic developer, while the negative one becomes insoluble in the organic developer.
- **Development:** the chemical change in polymer bonds allows some of the photoresist to be removed by a solution called developer.
- **Reactive Ion Etching (RIE):** a chemically reactive plasma removes the material deposited on the substrate, which isn't yet covered by the resist. The plasma is generated under low pressure by an electromagnetic field. High-energy ions of the plasma attack the wafer surface and react with it.

Instead of using the RIE, which is a dry process, one can utilize a *wet etching*: it consists of an immersion of the sample in a chemical solution, that removes the uppermost layer not protected by the resist mask. In Fig. 2.23 images at the Electronic Microscope of the four TI patterned films are shown.



**Fig. 2.23** Images at the Electronic Microscope of the four TI films (of different width of grating) after the EBL and RIE processes

## 2.6 Data Analysis and Fitting Models

### 2.6.1 The Drude-Lorentz Model

The optical conductivity of a metallic or insulating system can be decomposed into a sum of contributions related to different charge and lattice excitations. The Drude model derives from a classical analysis of the transport properties of a Fermi liquid, where the quasi-elastic scattering processes are controlled by one characteristic time. This leads to an optical conductivity of the form

$$\sigma_1(\omega) = \frac{\omega_p^2}{4\pi} \frac{\tau}{1 + (\omega\tau)^2} \quad (2.52)$$

where  $\omega_p = \sqrt{\frac{4\pi ne^2}{m}}$  is the plasma frequency of the Fermi liquid,  $n$  is the number of charge carriers for volume unit and  $m$  is the effective mass.

The Lorentz model, on the contrary, classically describes an insulator, where the atom can be modeled as a valence electron bound to a nucleus. The equation of motion of such a system is that of a driven damped harmonic oscillator, in which the driving force is due to the local electric field, while the damping is due to a dissipative term proportional to the velocity:

$$m \frac{d^2 \mathbf{r}}{dt^2} + m\gamma \frac{d\mathbf{r}}{dt} + m\omega_0^2 \mathbf{r} = -e\mathbf{E}_{loc} \quad (2.53)$$

In the linear response regime, the polarizability of the system  $\tilde{\alpha}(\omega)$  is

$$\mathbf{p} = \tilde{\alpha}(\omega)\mathbf{E}_{loc} = -e\mathbf{r} \quad (2.54)$$

where  $\mathbf{p}$  is the electric dipole. If one solves the Eq. 2.53, one obtains

$$\tilde{\alpha}(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2 - i\gamma\omega}. \quad (2.55)$$

As the polarizability is related to the dielectric function  $\tilde{\epsilon}(\omega)$  by

$$\tilde{\epsilon}(\omega) = 1 + 4\pi N\tilde{\alpha}(\omega)$$

where  $N$  is the number of oscillators per unit volume, one obtains

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} + \frac{4\pi Ne^2}{m} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (2.56)$$

with  $\epsilon_{\infty}$  equal to the dielectric function at high frequencies.

If the  $N$  oscillators have widths  $\gamma_j$  and resonance frequencies  $\omega_j$ , one can write

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} + \sum_{j=1}^N \frac{4\pi N_j e^2}{m} \frac{1}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega} \quad (2.57)$$

In Eq. 2.57, the contribution of free carriers, the so called Drude term, is obtained setting  $\omega_{0j} = 0$ , considering  $\omega_{0j}$  as the frequency of the transition from the electronic ground state to the excited state. Hence, the Drude term is

$$\tilde{\epsilon}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma_D\omega} = 1 - \frac{\tau\omega_p^2}{\tau\omega^2 + i\omega} \quad (2.58)$$

where  $\omega_p^2 = \frac{4\pi ne^2}{m}$  is the plasma frequency of free electrons and  $\tau = \frac{1}{\Gamma_D}$  is the average time between two electron-phonon, electron-impurity, electron-electron scattering provided by the Matthiessen rule [29]:

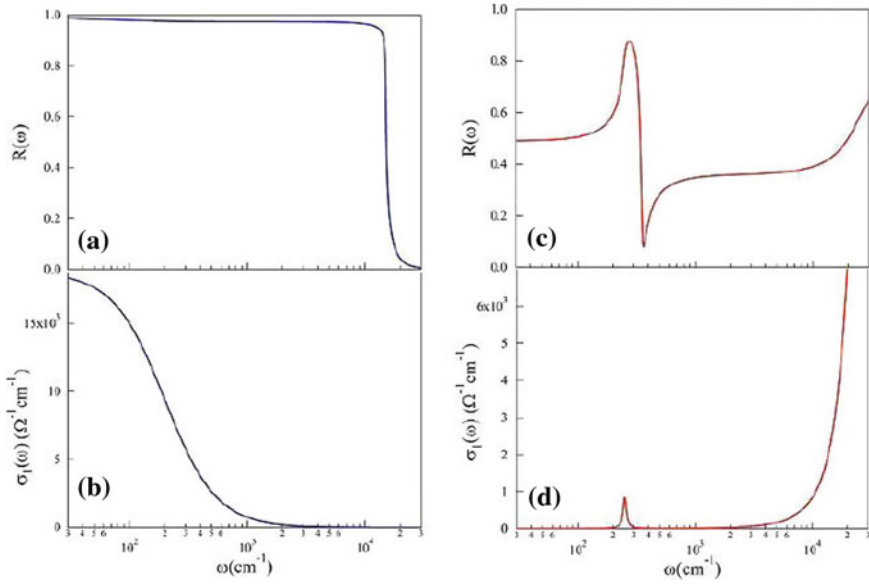
$$\frac{1}{\tau} = \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{e-imp}}. \quad (2.59)$$

If the system is a crystal, one has to add to 2.57 and 2.58 (Drude-Lorentz model) the contribution of the ions of the lattice to the polarizability. For instance, an ionic crystal with two atoms for unit cell, with equal mass and charge, that oscillate in an optic transverse normal mode (TO), has an electric dipole momentum, oscillating at the TO frequency. The related dielectric function is

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} + \sum_{k=1}^N \frac{4\pi N_k q^2}{M} \frac{1}{\omega_{0k}^2 - \omega^2 - i\gamma_k\omega} \quad (2.60)$$

where  $M$  and  $q$  are the mass and the charge of the ions, respectively, and  $\omega_{0k}$  are the vibration frequency of the lattice (associated with the phononic excitations), two or three order of magnitude lower than the electronic transition ones.

Then, the total dielectric function is



**Fig. 2.24** Reflectivity and optical conductivity calculated with the Drude-Lorentz model for: a metal with  $\omega_p = 15,000 \text{ cm}^{-1}$ ,  $\Gamma = 200 \text{ cm}^{-1}$  (a), (b); an insulator with a phonon ( $I_1^2 = 1,000 \text{ cm}^{-2}$ ,  $\gamma_1 = 20 \text{ cm}^{-1}$  and  $\omega_i = 250 \text{ cm}^{-1}$ ) and an optical electron transition in the visible range ( $I_2^2 = 100,000 \text{ cm}^{-2}$  and  $\omega_2 = 25,000 \text{ cm}^{-1}$ ) (c), (d)

$$\tilde{\epsilon}(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma_D\omega} + \sum_{j=1}^N \frac{S_{el,j}^2}{\omega_{0j}^2 - \omega^2 - i\gamma_j\omega} + \sum_{k=1}^{N'} \frac{S_{ph,k}^2}{\omega_{0k}^2 - \omega^2 - i\gamma_k\omega} \quad (2.61)$$

where  $S_{el,j}^2 = \frac{4\pi N_j e^2}{m}$ ,  $S_{ph,k}^2 = \frac{4\pi N_k q^2}{M}$ .

In Fig. 2.24a and b the reflectivity and the optical conductivity of a metal are shown as calculated through the Drude model for a good metal with  $\omega_p = 15,000 \text{ cm}^{-1}$  and  $\Gamma = 200 \text{ cm}^{-1}$ . The reflectivity presents a drop at the so called plasma edge frequency and the conductivity shows the Drude peak at  $\omega = 0$  having width proportional to  $\Gamma$ . In Fig. 2.24c and d the results for an insulator are shown: one can see a phononic peak ( $I_1^2 = 1,000 \text{ cm}^{-2}$ ,  $\gamma_1 = 20 \text{ cm}^{-1}$  and  $\omega_i = 250 \text{ cm}^{-1}$ ) and an optical electron transition in the visible range ( $I_2^2 = 100,000 \text{ cm}^{-2}$  and  $\omega_2 = 25,000 \text{ cm}^{-1}$ ).

### 2.6.2 Fano Model for the Optical Conductivity

The Fano theory describes the interaction of one or more discrete levels with a continuum of states, resulting in asymmetric optical absorption peaks [30]. Therefore, the optical conductivity, after the subtraction of the continuous electronic background,

has a Fano profile, given by the equation:

$$\tilde{\sigma}(\omega) = i\sigma_0 \frac{(q - i)^2}{i + (\omega^2 - \omega_T^2)/\gamma\omega} \quad (2.62)$$

where  $\gamma$  and  $\omega_T$  are the linewidth and the resonant frequency of the unperturbed vibrational state and  $q$  is the dimensionless Fano parameter. If  $\theta$  is the degree of asymmetry of the peak, one has

$$q = \frac{-1}{tg(\theta/2)} \quad (2.63)$$

For  $\theta = 0$ , or equivalently,  $|q| \rightarrow \infty$ , a Lorentzian line shape is recovered. While

- for  $\theta < 0$  ( $q > 0$ ),  $\omega_{ph} > \omega_{el}$ : a predominant interaction between the phononic mode and an electronic state lower in energy occurs.
- for  $\theta > 0$  ( $q < 0$ ),  $\omega_{ph} < \omega_{el}$ : a predominant interaction between the phononic mode and an electronic state higher in energy occurs.

Here,  $\omega_{ph}$  is the phonon frequency at  $k = 0$  and  $\omega_{el}$  is the central frequency of the electronic continuous state [31].

The oscillator strength  $S$  is also related to the Fano parameter by the relation:

$$S = 4\pi\sigma_0 \frac{(q^2 - 1)\gamma}{\omega_T^2} \quad (2.64)$$

One can account for the strong oscillator strength observed for the infrared-active phonons, by considering a linear coupling between lattice vibrations and electronic oscillators. For a phonon coupled to an electronic background, the optical conductivity is

$$\sigma_j(\omega) = \frac{-iA\omega}{(1 - \lambda_j)\omega_j^2 - \omega(\omega + i\gamma_j)} \quad (2.65)$$

where  $A = e_{T,j}^{*2}n_e/\mu$  and  $\lambda_j = g^2\epsilon_e/m_e\mu\omega_j^2\omega_{p,e}^2$  is a dimensionless electron-phonon coupling parameter. Moreover,

$$\epsilon_e = \frac{\omega_{p,e}^2}{\omega_e^2 - \omega(\omega + i\gamma_e)}$$

is the contribution to the dielectric function due to an electronic oscillator coupled to the phonons. The indexes  $e$  and  $j$  refer to the electronic oscillator and the  $j$ th phonon, respectively. In addition,

$$e_{T,j}^{*2} = \frac{\lambda_j\epsilon_en_i(Z_ie)^2\omega_j^2}{n_e\Omega_{ph}^2}$$

is the transverse effective charge where  $\Omega_{ph}^2 = 4\pi n_i (Z_i e)^2 / \mu$  is the square plasma frequency of the lattice, with  $Z_i$  the formal valence of the ions. The Fano asymmetry parameter  $\theta$  is

$$\theta_j = 2 \text{Arg}[\epsilon_e(\omega_j)]. \quad (2.66)$$

### 2.6.3 Fano Resonance in the Extinction Coefficient

In the previous section, we have seen that the Fano theory describes the interference between one or more discrete states (DS) with a continuum of states (CS) (usually an electronic background). In particular, one can observe a Fano resonance when vibrational excitations of a molecule are coupled with a plasmon resonance in surface-enhanced IR absorption [32].

A peculiar characteristic of these resonances is their asymmetric line profile, due to the coexistence of constructive and destructive interference processes. Recently, it has been shown that these phenomena are observable in plasmonic nanostructures [33–37]. In this case the plasmon resonance (PR) acts as the CS and interferes with a DS: the DS can be the excitation of a guided mode, the excitation of a diffraction channel (like a grating or an array), the excitation of a dark (not excited) plasmon mode, the vibrational (active or not IR active) excitation.

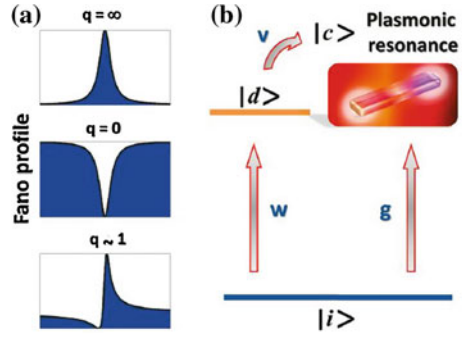
Although Fano interference has been known for more than fifty years, there is still a gap between theory and experimental results when plasmonic resonances are involved. Generally, the approach to analyze such an asymmetry is to fit it with a Fano profile (see Sect. 2.6.2), by applying the scattering matrix method and considering all the involved channels as discrete levels. Another possibility consists in using a classical phenomenological method of coupled oscillators.

There is a further method that is able to explain how the energy width of the PR and the energy separation between the PR and the DS, together with their coupling strength, may affect this asymmetric profile. This method can be used for fitting macroscopic optical functions like transmittance and reflectance and will be utilized in Sect. 3.4.2. In Fig. 2.25b one can see a sketch where a plasmonic resonance, with eigenstate  $|c\rangle$  and acting as the CS, interferes with a discrete state  $|d\rangle$  with a coupling constant  $v$  and each one interacts with an incident state (of an electromagnetic field)  $|i\rangle$  by  $g$  and  $w$ , respectively. The result is a new mixed state that accounts for both excitations paths. Performing exact calculations of the probability of exciting that mixed state, one can obtain a simple analytical description of Fano resonances mediated by PRs [32]. Considering the extinction coefficient, defined as

$$\epsilon(\omega) = 1 - T(\omega) \quad (2.67)$$

where  $T(\omega)$  is the transmittance, one can write for the shape of the resonance, caused by the coupling between a DS and a CS, the following equation:

**Fig. 2.25** Different Fano line-shapes for three values of the asymmetry parameter  $q$  (a). Fano process with a plasmonic continuum state: an incident state  $|i\rangle$  excites a quasi-continuum state obtained from the interaction of a plasmonic resonance,  $|c\rangle$ , with a discrete state  $|d\rangle$ . The interaction is described by the coupling factors  $w$ ,  $g$  and  $v$  (b) [32]



$$\epsilon(\mathcal{E}) = \frac{(\mathcal{E} + q)^2}{\mathcal{E}^2 + 1} \quad (2.68)$$

where  $q$  is the Fano factor, related also to the excitation probability ratio between the discrete and the continuum state and  $\mathcal{E}$  is the reduced energy, defined by

$$\mathcal{E} = \frac{2(\hbar\omega - \hbar\omega_{ph})}{\Gamma_{ph}} \quad (2.69)$$

It depends on

- $\omega$ : frequency of the incident photon.
- $\omega_{ph}$ : frequency of the discrete state (a phonon in the specific case in Fig. 2.14).
- $\Gamma_{ph}$ : width of the discrete state.

In Fig. 2.25a the three special case for the Fano profile are reported:  $q \rightarrow \infty$ ,  $q = 0$ ,  $q$  finite. In the first case, the probability of directly exciting the continuum is small and the profile is mainly determined by the transition through the discrete mode (Lorentzian shape of, for example, a phonon); in the second case, a symmetric antiresonance arises, known as Breit-Wigner dip [38]; in the third case, an asymmetric line-shape does appear.

In order to include the dependence from the PR feature in Eq. 2.68, now we consider that the coupling to the CS is governed by the excitation of a PR. If  $\mathcal{H}_0$  is the unperturbed Hamiltonian, it has an eigenstate  $|d\rangle$  with eigenvalue  $E_{ph}$  ( $E_{ph} = \hbar\omega_{ph}$ ) and one,  $|c\rangle$ , with a continuum spectra of eigenvalues  $E$  ( $E = \hbar\omega$ ). If, then,  $V$  is the Hamiltonian which couples  $|d\rangle$  with  $|c\rangle$ , one can write (supposing  $\hbar = 1$ ):

$$\langle d | \mathcal{H}_0 | d \rangle = \omega_{ph} \quad (2.70)$$

$$\langle c | \mathcal{H}_0 | c' \rangle = \omega \delta(\omega - \omega') \quad (2.71)$$

$$\langle c | V | d \rangle = v \sqrt{\mathcal{L}(\omega)} \quad (2.72)$$

$$\langle d | V | d \rangle = 0 \quad (2.73)$$

$$\langle c | V | c \rangle = 0 \quad (2.74)$$

One can see how the coupling between  $|c\rangle$  and  $|d\rangle$  is determined both by the coupling constant  $v$  and by the plasmonic line-shape  $\mathcal{L}(\omega)$ , which is supposed to be Lorentzian, that is

$$\mathcal{L}(\omega) = \frac{1}{1 + \left(\frac{\omega - \omega_p}{\Gamma_p/2}\right)^2} \quad (2.75)$$

where

- $\omega_p$  is the frequency of the plasmon resonance.
- $\Gamma_p$  is the width of the plasmon resonance.

If  $\mathcal{H} = \mathcal{H}_0 + V$  is the total Hamiltonian, we can solve the eigenvalue problem  $\mathcal{H}|\Psi\rangle = E|\Psi\rangle$ , where  $|\Psi\rangle$  is the new mixed state quasi-CS. If, then, we consider an incident photon in the DS  $|i\rangle$ , we have a coupling by an Hamiltonian  $W$  with the state  $|d\rangle$  and  $|c\rangle$ , that is

$$\langle i|W|d\rangle = w \quad (2.76)$$

$$\langle i|W|c\rangle = g\sqrt{\mathcal{L}(\omega)} \quad (2.77)$$

where  $w$  and  $g$  are the coupling factors.

We can recover the Fano profile by solving the previous problem, i.e. by calculating the probability  $|\langle i|W|\Psi\rangle|^2$  that a photon in state  $|i\rangle$  excites a quasi-CS state  $|\Psi\rangle$ . Hence, by normalizing the latter result with the probability of exciting the continuum PR in the absence of the DS, we obtain the same result as in Eq. 2.68, namely

$$\frac{|\langle i|W|\Psi\rangle|^2}{|\langle i|W|c\rangle|^2} = \frac{(\mathcal{E} + q)^2}{\mathcal{E}^2 + 1} \quad (2.78)$$

with, now,  $q$  and  $\mathcal{E}$  related also to the width and the energy position of the PR, that is

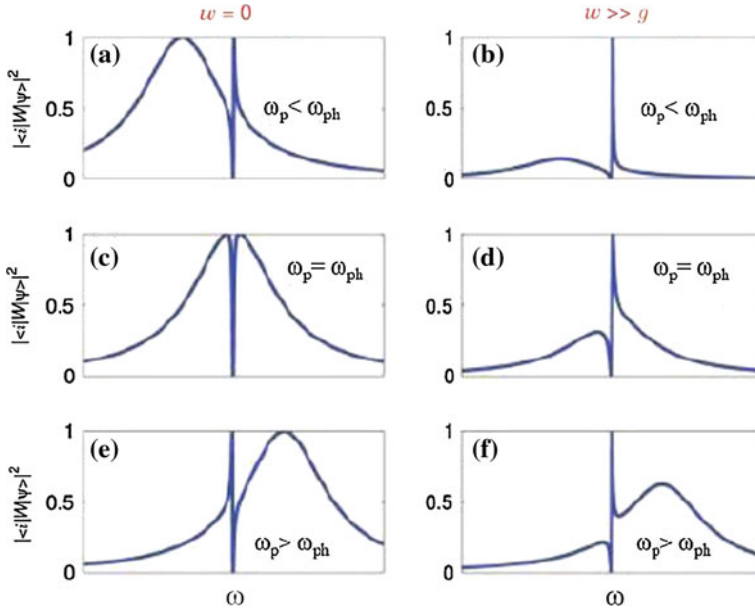
$$q(\mathcal{E}) = \frac{vw/g}{\Gamma_{ph}(\omega)/2} + \frac{\omega - \omega_p}{\Gamma_p/2} \quad (2.79)$$

$$\mathcal{E} = \frac{\omega}{\Gamma_{ph}(\omega)/2} - \frac{\omega - \omega_p}{\Gamma_p/2} \quad (2.80)$$

Here, in particular,

$$\Gamma_{ph}(\omega) = 2\pi v^2 \mathcal{L}(\omega) \quad (2.81)$$

relating the energy width of the DS to the coupling constant  $v$  to the PR line shape. In particular this means that the lifetime  $1/\Gamma_{ph}$  of the discrete state is completely determined by its coupling with the continuous state. When  $V$  is small compared with  $\mathcal{H}_0$ ,  $\Gamma_{ph}(\omega)$  coincides with the decay rate of the DS: in absence of interaction between DS and CS, if DS is an IR active mode, it should have a not zero width  $\Gamma'_{ph}$ .



**Fig. 2.26** Fano resonances calculated from Eq. 2.78–2.79 for two different coupling regimes  $w = 0$  (a), (c), (e) and for  $w \gg g$  (b), (d), (f), when a DS with frequency  $\omega_{ph}$  interacts with a continuum plasmon state with frequency  $\omega_p$  ( $\Gamma_p = 10\Gamma_{ph}$ ) for different relative positions [32]

The dependence of  $q$  and  $\mathcal{E}$  on the parameter  $\omega, \omega_p, \Gamma_p, \Gamma_{ph}$  and the three coupling factors,  $v, w, g$ , explains why the Fano resonance exhibits different degrees of asymmetry.

One can distinguish two main cases (see Fig. 2.26):

- $w \ll v, g$  : the line-profile is mainly determined by the PR, which is modified by the coupling to the DS ( $v$ ). Indeed, the DS mainly excites indirectly through the plasmonic state. As the minimum of the Fano resonance always lies between the two maxima, the one of the DS (phononic peak) and the other one of the plasmonic state, in the case of  $w = 0$  and  $\omega_p = \omega_{ph}$  a symmetric dip is obtained.
- $w \gg g$  : the interaction with the CS mainly goes through the DS, then the main obtained resonance is that of the DS (phononic peak), particularly in the case  $\omega_p < \omega_{ph}$ .

Therefore, it is rather simple to understand which coupling regime holds. This model will be used in Chap. 3 to explain the plasmonic spectra observed in topological patterned films of  $\text{Bi}_2\text{Se}_3$ .

## References

1. J.S. Nodvick, D.S. Saxon, Phys. Rev. **96**, 180 (1954)
2. R.L. Warnock, P. Morton, Particle Accelerators **25**, 113 (1990)
3. J.B. Murphy, S. Krinsky, R.L. Gluckstern, Particle Accelerators, **57**, 9 (1997)
4. M. Abo-Bakr, J. Feikes, K. Holldack, G. Wüstefeld, H.-W. Hübers, Phys. Rev. Lett. **90**, 254801 (2003)
5. M. Abo-Bakr, J. Feikes, K. Holldack, P. Kuske, W.B. Peatman, U. Schade, G. Wüstefeld, H.-W. Hübers, Phys. Rev. Lett. **90**, 094801 (2003)
6. M. Venturini, R. Warnock, Phys. Rev. Lett. **89**, 224802 (2002)
7. A.J. LaRocca, in *The Infrared Handbook*, ed. by G. Zissis, W. Wolfe for IRIA, chap2 (1978)
8. F.J. Studer, R.F. Van Beers, J. Opt. Soc. Am. **54**, 945 (1964)
9. J.E. Chamberlain, G.W. Chantry, F.D. Findlay, H.A. Gebbie, J.E. Gibbs, N.W.B. Stone, A.J. Wright, Infrared Phys. **6**, 195 (1966)
10. C.C. Homes, M. Reedik, D.A. Cradles, T. Timusk, Appl. Optics **32**, 2976 (1993)
11. F. Wooten, *Optical Properties of Solids* (Academic Press, New York, 1972)
12. M. Dressel, G. Grüner, *Electrodynamics of Solids* (Cambridge University Press, Cambridge, 2002)
13. H.A. Kramers, Nature (London) **117**, 775 (1926)
14. H.A. Kramers, in *Estratto dagli Atti del Congresso Internazionale di Fisica*, vol. 2 (Zanichelli, Bologna, 1927), p. 545
15. H.A. Kramers, *Collected Scientific Papers* (North-Holland, Amsterdam, 1956)
16. R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926)
17. R. de L. Kronig, Ned. Tijdschr. Natuurk. **9**, 402 (1942)
18. P.F. Henning, C.C. Homes, S. Maslov, G.L. Carr, D.N. Basov, B. Nikolić, M. Strongin, Phys. Rev. Lett. **83**, 4880 (1999)
19. S.A. Maier, *Plasmonics: Fundamentals and Applications* (Springer, New York, 2007)
20. P.W. Milonni, *Fast Light, Slow Light and Left-Handed Light* (Institute of Physics Publishing, Bristol, 2005)
21. W.L. Barnes, A. Dereux, T.W. Ebbesen, Nature **424**, 824 (2003)
22. W. Zhang, Eur. Phys. J. Appl. Phys. **43**, 1 (2008)
23. G. Goubau, J. Appl. Phys. **21**, 1119 (1950)
24. J.B. Pendry, L. Martin-Moreno, F.J. Garcia-Vidal, Science **305**, 847 (2004)
25. Y.S. Hor, A. Richardella, P. Roushan, Y. Xia, J.G. Checkelsky, A. Yazdani, M.Z. Hasan, N.P. Ong, R.J. Cava, Phys. Rev. B **79**, 195208 (2009)
26. S. Jia, H. Ji, E. Climent-Pascual, M.K. Fuccillo, M.E. Charles, J. Xiong, N.P. Ong, R.J. Cava, Phys. Rev. B **84**, 235206 (2011)
27. R. Valdés Aguilar, A.V. Stier, W. Liu, L.S. Bilbro, D.K. George, N. Bansal, L. Wu, J. Cerne, A.G. Markelz, S. Oh, N.P. Armitage, Supplemental Materials for: Phys. Rev. Lett. **108**, 087403 (2012)
28. N. Bansal, Y.S. Kim, M. Brahlek, E. Edrey, S. Oh, Phys. Rev. Lett. **109**, 116804 (2012)
29. N.W. Ashcroft, D. Mermin, *Solid State Physics* (Saunders College Publishing, New York, 1976)
30. U. Fano, Phys. Rev. **124**, 1866 (1961)
31. A. Damascelli, K. Schulte, D. van der Marel, A.A. Menovsky, Phys. Rev. B **55**, R4863 (1997)
32. V. Giannini, Y. Francescato, H. Amrania, C.C. Phillips, S.A. Maier, Nano Lett. **11**, 2835 (2011)
33. F. Hao, Y. Sonnefraud, P. Van Dorpe, S.A. Maier, N.J. Halas, P. Nordlander, Nano Lett. **8**, 3983 (2008)
34. N. Verellen, Y. Sonnefraud, H. Sobhani, F. Hao, V.V. Moshchalkov, P. Van Dorpe, P. Nordlander, S.A. Maier, Nano Lett. **9**, 1663 (2009)
35. L.A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N.J. Halas, V.N. Manoharan, P. Nordlander, G. Shvets, R. Capasso, Science **328**, 1135 (2010)
36. I.M. Pryce, K. Aydin, Y.A. Kelaita, R.M. Briggs, H.A. Atwater, Nano Lett. **10**, 4222 (2010)
37. Y. Sonnefraud, N. Verellen, H. Sobhani, G. Vandenbosch, V. Moshchalkov, P. Van Dorpe, P. Nordlander, S.A. Maier, ACS Nano **4**, 1664 (2010)
38. A. Miroshnichenko, S. Flach, Y. Kivshar, Rev. Mod. Phys. **82**, 2257 (2010)

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