Applications of UV-Raman Spectroscopy to Microelectronic Materials and Devices

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Abstract. Raman spectroscopy is a powerful technique for characterization of microelectronic materials and device structures. However, the commonly used visible Raman spectroscopy technique is severely limited in both lateral and depth resolution in applications to rapidly shrinking ULSI device structures. The UV micro-Raman technique can greatly enhance the spatial resolution by taking advantage of the shorter wavelength and much smaller optical penetration depth (≈10 nm in Si at 325 nm versus 400 nm in the visible). We present UV micro-Raman mapping of stress and crystallinity in shallow trench isolated (STI) CMOS devices. The shorter optical penetration depth in Si and other wide-gap materials also makes UV-Raman spectroscopy very appealing in characterizing thin films of such materials. Examples will be given in characterization of ultrathin strained Si channels on SiGe buffer and thin SrTiO$_3$ and SiN dielectric films on Si.

INTRODUCTION

Raman spectroscopy has proven to be an extremely useful tool for characterizing semiconductor materials and devices [1–3]. Raman scattering from lattice vibrations and electronic excitations is very sensitive to the local environment and can provide information about material and physical properties on the scale of a few lattice spacings. This technique is widely used as a nondestructive and quantitative tool to analyze mechanical stress, crystallinity, composition, nanostructures, carrier concentration, and mobility in semiconductor materials. Integration of an optical microscope with a Raman setup provides micro-probing capability. By using a sub-micron precision sample translation stage and multichannel optical detection, one-dimensional Raman scanning and two-dimensional Raman mapping can easily be performed on device structures with steps as small as ≈0.1 μm.

The rapid downscaling of IC devices and emerging new IC technologies, however, posts great challenges to the most commonly used visible Raman spectroscopy. Further improvement of the lateral spatial resolution of micro-Raman spectroscopy requires the migration from a visible to a UV laser source with a conventional optical microscope. For example, one can reduce the focused laser spot size from 0.7 μm to 0.45 μm by changing the laser line from 514 nm to 325 nm using a 100x objective with a numerical aperture of 0.90. Moreover, the much shorter optical penetration depth in the UV (≤10 nm at 325 nm in Si) allows probing shallow active layers in CMOS devices, which is impossible with a visible laser due to the much larger penetration depth (~1 μm at 500 nm wavelength).

UV-Raman spectroscopy has shown great advantages in Raman mapping of stress and crystallinity in Si-based devices.

The larger photon energy also makes UV-Raman scattering a crucial tool to characterize thin wide-gap films, such as GaN, SiC, SrTiO$_3$, Si-rich silicon nitride and other dielectric films. Care must be taken, however, to ensure that the intense UV radiation does not cause damage to the material. We have had only limited success with UV Raman spectroscopy of GaAs and related compounds due to irreversible changes of the samples after UV exposure. The shallow penetration depth also has the disadvantage that buried layers often cannot be analyzed.

EXPERIMENT

UV-Raman measurements were carried out in backscattering geometry at room temperature using the UV (320 nm) line of a He-Cd laser. The incident laser beam of ~1.0 mW power was focused by a 100x UV-grade objective (0.9 NA) to about 0.5 μm in diameter on the sample surface. The scattered light was collected by the same objective, analyzed, and detected by a UV-upgraded Dilor XY 800 triple monochromator with three 2400 lines/mm gratings blazed at 300 nm and a 2048x512 (pixel size of 13.5 μm$^2$) back-illuminated low-noise UV CCD detector cooled by LN$_2$. Both normal and high resolution modes of the spectrometer were used, where the first and second stages were subtractively and additively coupled, with spectral resolutions of about 5.5 and <2 cm$^{-1}$, respectively. By curve fitting, peak shifts of ≤0.1 cm$^{-1}$ can be resolved in high-resolution mode.
CHARACTERIZATION OF Si-BASED MICROSTRUCTURES

Micro-Raman spectroscopy is widely utilized for characterization of local stress [4,5] and crystallinity in semiconductor microstructures, since conventional x-ray diffraction lacks lateral and depth resolution and transmission electron microscopy is destructive. Local mechanical stress can have a huge impact on device performance and reliability. Stress is often generated in semiconductors by device fabrication processing, such as polishing, etching, annealing, and by mismatch in lattice constants or thermal expansion coefficients between different layers. Stress is measured by Raman scattering from an optical phonon, whose frequency is shifted from the unstrained value due to stress because of the non-harmonicity of the lattice. Strain-free crystalline Si has a cubic diamond crystal structure and three degenerate phonon modes at the Brillouin zone center (q=0), where the first-order Raman scattering takes place as required by momentum conservation. The Raman tensors for the three modes are

\[
R(TO_1) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}, \quad R(TO_2) = \begin{pmatrix} 0 & 0 & d \\ 0 & d & 0 \\ d & 0 & 0 \end{pmatrix},
\]

\[
R(LO) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix},
\]

where TO and LO denote transverse and longitudinal optical phonons, respectively. Note that for zincblende-type crystals such as GaAs, the degeneracy of the LO and TO phonons at q=0 is lifted by the internal electric field associated with the LO phonon mode. Hydrostatic strain shifts the phonon frequencies without altering the symmetry of the crystal, while anisotropic strain, due to uniaxial or biaxial stress, alters the crystal symmetry and thus lifts certain phonon mode degeneracies (splittings). Because strain in a semiconductor microstructure presents as second rank tensor \( \varepsilon \), the determination of all strain components can be very complicated. This not only requires measuring all three phonon frequencies, which is almost impossible for real device structures, but also solving the dynamic secular matrix equation to correlate the phonon frequencies and strain components. Therefore, approximations are used in stress analysis of microstructures. For example, one often uses the planar stress model with an isotropic biaxial stress \( \sigma \) applied in the plane parallel to the substrate surface [6]:

\[
\sigma = \begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{pmatrix}.
\]

This model holds exactly for heteroepitaxial layers such as Si/SiGe heterostructures, since there is no force along the surface normal. The strain tensor is then [6]

\[
\varepsilon = \sigma \begin{pmatrix} S_{11} + S_{12} & 0 & 0 \\ 0 & S_{11} + S_{12} & 0 \\ 0 & 0 & 2S_{12} \end{pmatrix},
\]

where \( S_{11} \) and \( S_{12} \) are the elastic compliance constants. The strain (stress) induced frequency shifts for the LO and TO phonons for the two-dimensional biaxial stress are given by [6]

\[
\omega_{LO} - \omega_0 = \frac{1}{2\omega_0} \left( \frac{S_{12}}{S_{11} + S_{12}} \right) \left( p + q \right) \varepsilon_{yy},
\]

and

\[
\omega_{TO} - \omega_0 = \frac{1}{2\omega_0} \left( \frac{2S_{12}}{S_{11} + S_{12}} \right) q \varepsilon_{yy},
\]

where \( \omega_0 \) is the unstrained phonon frequency, \( p \) and \( q \) are phonon deformation potentials. They are also often written as

\[
\omega_{LO} - \omega_0 = b_{LO} \varepsilon_{yy} = b_{LO} (S_{11} + S_{12}) \sigma
\]

and

\[
\omega_{TO} - \omega_0 = b_{TO} \varepsilon_{yy} = b_{TO} (S_{11} + S_{12}) \sigma,
\]

where \( b_{LO} \) and \( b_{TO} \) are called the strain-shift coefficients for the LO and TO phonons. Using \( p/\omega_0^2 = -1.85 \) and \( q/\omega_0^2 = -2.31 \) (\( \omega_0 = 520 \text{ cm}^{-1} \)) obtained by piezo-Raman spectroscopy [7], \( \varepsilon_{yy} = 76.8 \times 10^{-14} \text{ cm}^2/\text{dyne} \) and \( S_{12} = -21.4 \times 10^{-14} \text{ cm}^2/\text{dyne} \) as calculated from the Si elastic constants [8], one obtains \( b_{LO} = 830 \text{ cm}^{-1} \), \( b_{TO} = 618 \text{ cm}^{-1} \), and \( (S_{11} + S_{12})^{-1} = 180 \text{ GPa} \). For back-scattering off the (001) surface of a diamond- or zincblende-type crystal, only the LO phonon is allowed for the incident and scattered polarizations parallel to the [110] or [1-10] axes, or for crossed polarizations along the [100] or [010] axes. This also holds when the crystals are under a tetragonal strain. One can see from Eqs. (4) and (6) that compressive planar (biaxial) stress results in phonon hardening (frequency increase) and tensile stress leads to phonon softening (frequency decrease).

As a first example, we present the results of stress analysis of shallow trench isolation (STI) structures. Effects of stress become increasingly important with
decreasing IC device size. In front-end CMOS fabrication, stresses are introduced by STI and gate-stack processing. To achieve a high device density in ultra large-scale integration (ULSI), shallow trench isolation has replaced local oxidation of Si (LOCOS) isolation used for very large-scale integration (VLSI) devices. To investigate stress due to STI, we carried out Raman studies of STI structures of various sizes on bulk Si and SOI substrates after each STI process step with 1-D Raman scanning and 2-D Raman mapping. It was found that the stress distribution varies with processing and depends on the substrate (bulk or SOI), trench shape, and size.

Figure 1 shows stress variations obtained by 1-D Raman scanning across a line test structure with 1.5 μm active and 1.5 μm trench widths on bulk Si and SOI after trench sacrificial oxide deposition. There are drastic effects of the substrate type (bulk Si or SOI) on the stress field. The trench regions for both substrates are unstrained or slightly compressively stressed. The edges of the active region are under strong compressive stress, and the stress is released slightly away from the edges into the active areas for the bulk Si substrate. In case of the SOI substrate, the stress is relaxed rapidly away from the edges and almost fully relieved in the middle parts of the active regions.

Figure 2 shows stress variation across three STI line structures with different active and trench widths on a bulk Si substrate. One can see from Fig. 2 (top) that the wide trench (1.5 μm) areas are under a slight tensile stress, and the active regions under compressive stress without relaxation due to the narrow active width (0.18 μm). The observed stress could be smaller than the real stress because the laser spot is larger than the active width. In case of wide active (1.5 μm) and narrow trench (0.21 μm) regions (center), since the trench is narrower than the laser spot, the stress in the almost fully relaxed trench could not be resolved. In the center
of the active regions, stress is relieved by about 80 MPa. It is striking to see that our UV micro-Raman system can resolve the 0.27/0.30 μm structure (bottom), even though the peaks and valleys of the stress are smoothed to some extent by averaging the active and trench areas within the laser spot.

FIGURE 3. (a): Optical image of a device structure after STI process; (b): Stress image obtained with 2-D Raman mapping of the marked area.

Two-dimensional (2-D) UV micro-Raman mapping allows lateral stress imaging of device structures. Figure 3 displays the stress image of the marked area in a device structure after STI. The stress depends on both shape and size of the active region. The Raman data provide a unique input and validity check for device stress simulations, which play an important role in device stress engineering in ULSI design and process optimization.

CHARACTERIZATION OF HIGH-MOBILITY STRAINED SI CMOS

UV-Raman spectroscopy has demonstrated great advantages in characterizing Si/SiGe heterostructures, which are extremely useful in extending and elevating current Si technology. For example, SiGe-based heterojunction bipolar transistors (HBTs) have been used to enhance the frequency of BiCMOS (Bipolar CMOS) bipolar transistors for wireless applications, and strained Si channel (SSC) CMOS is used to improve FET speed. UV-Raman spectroscopy has demonstrated great advantages in characterizing Ge composition or strain in ultrathin SiGe layers (~30 nm) in HBTs and Si channels (~10 nm) in SSC CMOS.

FIGURE 4. Raman spectra (a) and frequency (b) of the Si-Si LO phonon mode in 30 nm SiGe films with different Ge contents (x) on Si, in comparison with bulk Si. The line shows a linear fit to the data (symbols).

Figure 4(a) shows Raman spectra of the Si-Si LO phonon peak in a series of 30 nm thick SiGe films with different Ge contents compared to a bulk Si reference. The short penetration depth of the UV laser allows an accurate measurement of the phonon frequencies, which are plotted in Fig. 4(b) as function of Ge fraction x. The experimental data can be fitted with a linear function:

\[ \omega(x) = 520.71 - 31.28x, \]
which represents the dependence of the LO phonon frequency on Ge content for fully strained SiGe on Si. The slope of Eq. (8) is slightly larger than 29.99 cm$^{-1}$, determined using a visible laser at 514.5 nm [9]. This difference between the UV and visible Raman results could be caused by a larger uncertainty in the visible Raman measurement (where the strong Si substrate peak overlaps with the smaller SiGe peak) or by the dependence of the phonon strain shift coefficient in Eq. (6) on laser wavelength.

Figure 5 displays spectra from a 15 nm strained Si film grown epitaxially on a thick relaxed SiGe buffer on Si in comparison with a bulk Si reference. No signal from the SiGe layer appears (due to the shallow penetration depth of the laser) and thus good accuracy for the strain in the Si channel can be achieved. 2-D Raman mapping has also been used to image the lateral strain field of the strained Si layer, which follows the cross-hatch topography pattern seen by atomic force microscopy (AFM) [10].

In addition to characterizing strain, crystallinity and composition in thin layers, the short penetration depth also makes UV micro-Raman spectroscopy useful for depth profiling of Si/SiGe heterostructures by line scans on samples beveled at a shallow angle. These results will be published elsewhere.

**CHARACTERIZATION OF WIDE GAP THIN FILMS ON Si**

The larger laser photon energy makes UV Raman spectroscopy an ideal tool for characterizing thin wide-gap films, such as GaN, SiC, SrTiO$_3$, and other dielectric films.

As one example, we discuss characterization of epitaxial SrTiO$_3$ films with UV Raman spectroscopy. SrTiO$_3$ is of great interest due to its potential applications in MOSFETs as an alternative gate oxide [11], in compliant substrates as a buffer layer [12], and in frequency agile devices with ferroelectric tunability [13]. The small optical penetration depth (~26 nm) at 3.8 eV photon energy (above the band gap of SrTiO$_3$ at 3.4 eV) allows us to measure epitaxial SrTiO$_3$ films on Si as thin as 10 nm. Figure 6 shows Raman spectra of a 20 nm film grown epitaxially with molecular beam epitaxy (MBE) on Si and bulk single crystal SrTiO$_3$ for comparison. The Raman spectrum of the thin film appears noticeably different from bulk single crystal. Since there is no Raman-active mode in the perovskite crystal structure, only the second-order phonon features are seen for bulk SrTiO$_3$. Similar two-phonon Raman features also dominate the Raman spectra of the MBE SrTiO$_3$ films, indicating rather good crystallinity. However, additional weak peaks emerge at about 180, 470, 540, and 790 cm$^{-1}$, corresponding to the positions of the LO$_1$ or TO$_2$, LO$_3$, TO$_3$, and LO$_3$ modes. These Raman-forbidden modes are activated by defects or lattice distortion in the films [12].

Amorphous silicon nitride films are essential in the semiconductor industry and have a variety of applications, e.g., as a diffusion barriers for H$_2$O and sodium, as passivation layers, antireflection coatings, oxidation masks, or gate and capacitor dielectrics. Such applications are made possible by the fact that nitrides can be tailored by varying the composition to obtain desired electrical, optical, and mechanical properties. We have found that UV Raman scattering is a powerful tool to study the microstructure of excess Si in the films.
increasing Si content, the SiN energy gap decreases and nano-Si clusters are formed. Raman spectra from two Si-rich nitride films deposited with low-pressure chemical vapor deposition (LPCVD) are plotted in Fig. 7. The Si/N ratio is 1.21 and 0.81, respectively, determined by Rutherford backscattering (RBS), larger than the stoichiometric value of 0.75 for Si$_3$N$_4$. A spectroscopic ellipsometry (SE) study of the same films showed that the films have a Tauc-Lorenz gap of 2.17 and 3.24 eV, respectively, corresponding to Si/N ratios of 0.97 and 0.87 according Jellison and coworkers [14]. The different value derived from the SE data in [14] may be caused by a different microstructure in the films. The Raman bands between 100 and 500 cm$^{-1}$ in Fig. 7 indicate a large amount of a-Si clusters formed in the film with higher Si/N ratio. The presence of such a-Si clusters in the films can affect the optical, mechanical, and electrical properties.

**FIGURE 7.** Raman spectra of LPCVD silicon-rich nitride films with Si/N ratios of 1.21 and 0.81. Note that the Si/N ratio equals 0.75 for stoichiometric nitride Si$_3$N$_4$ with an energy gap of 4.4 eV.

**SUMMARY**

UV Raman spectroscopy has proven to be a unique and powerful tool for characterization of materials and devices in ULSI technology. The much shorter UV optical penetration depth in Si allows characterization of stress and crystallinity in thin active layers and heterostructures in modern Si-based technology. The larger photon energy also makes this technique an ideal tool to study thin wide-gap films on Si.

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