In Situ Optical Diagnostics of Silicon Chemical Vapor Deposition Gas-Phase Processes

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Abstract. During silicon thermal chemical vapor deposition, reactions occurring in the gas phase above the wafer surface can strongly influence the deposited film quality. Depending on process conditions (e.g., temperature, silicon precursor, carrier gas, pressure) gas phase reactions can include not only precursor decomposition but also nucleation of silicon nano-particles above the wafer surface. Optical diagnostics were employed to investigate such processes during silicon chemical vapor deposition via silane pyrolysis. Measurements were performed in a vertical flow, rotating disk reactor under various process conditions. Gas phase silicon particle spatial distributions were determined with elastic light scattering. Chemical composition of the particles was investigated in situ with vibrational Raman spectroscopy. Raman spectra showed that the particles were composed of amorphous silicon and/or crystalline silicon, depending on growth temperature. Raman spectral features of the crystalline silicon also indicated crystalline domain sizes in the ca. 3 nm to ca. 10 nm size range. Gas phase temperature measurements (in the absence of particles) were used to estimate an amorphous-to-crystalline silicon transition temperature of ca. 866 K.

INTRODUCTION

Despite the wide technical relevance of silicon thermal chemical vapor deposition (CVD), the gas phase chemical and physical mechanisms involved in this process are not completely understood. Although general trends have been well characterized, e.g., relationships between deposited film quality and gas phase parameters [1], the mechanisms underlying these relationships have not yet been fully established. This is unfortunate in that a better understanding of this process could aid in improvement of film deposition procedures (for silicon and related materials) and CVD reactor design. Hence, further investigation of gas phase reactions involved in silicon thermal CVD processes could be beneficial.

Gas phase processes of particular interest in thermal CVD include reactant depletion and diffusion, as well as gas phase nucleation and transport of solid particles. In addition, these processes typically occur in the presence of large temperature gradients. Therefore, when investigating CVD processes, spatially resolved probes of gas phase temperature, species concentrations, and particle formation and transport are desirable. However, due to the intimate relationship between deposited film properties and reactor process parameters, system properties must not be perturbed during an investigation. These factors make optical diagnostics attractive for CVD investigations. One such diagnostic is Raman spectroscopy. Investigations employing Raman spectroscopy to probe species concentrations and/or temperatures under silicon thermal CVD conditions have been reported, e.g., [2-6]. However, none of these investigations have involved the in situ characterization of gas phase nucleated particles, the purpose of the work described here.

In this work, in situ Raman spectra of gas phase nucleated particles formed during silane pyrolysis were collected as a function of wafer surface temperature in a thermal CVD reactor. The Raman spectra showed that the particles were composed of amorphous silicon (a-Si) and/or crystalline silicon (c-Si), depending on growth temperature. Raman spectral features of the c-Si also indicated crystalline domain sizes in the ca. 3 nm to ca. 10 nm size range.
Gas phase temperature (in the absence of particles) was determined from nitrogen pure rotational Raman spectra and used to estimate an amorphous-to-crystalline silicon transition temperature of ca. 866 K. The work described here is one aspect of a broader investigation of silicon thermal CVD that involves experimental measurement of gas phase temperatures and species concentrations, and numerical modeling of gas phase chemistry and flow and aerosol dynamics [5-8].

**EXPERIMENTAL TECHNIQUE**

The CVD reactor is based on a previously reported design [6]. The process gases are injected at the top, flow through a stainless steel mesh into the 10 cm internal diameter quartz tube and are exhausted through the bottom of the reactor. A 50 mm diameter silicon wafer rests in the recess of molybdenum susceptor that is inductively heated with a 5 kW RF power supply. The distance from the mesh to the susceptor is 15 cm. A type K thermocouple in contact with the susceptor base is used in the control of the RF power supply output to maintain the susceptor temperature. Nominal thermocouple temperatures were varied from 823 K to 1100 K. Thermocouple temperature expanded uncertainties (with a coverage factor of 2) were estimated from the thermocouple manufacturer's specifications. Two gas compositions (by volume) were employed in this work: 0.86 % mole fraction silane/10 % mole fraction nitrogen/balance helium (SiH4/N2/He) and 10 % mole fraction nitrogen in a balance of helium (N2/He). All gases were purified with bulk gas purifiers prior to injection into the reactor. The nominal total gas flow rate was 15 L/min. All gas delivery lines were constructed of electropolished stainless steel tubing. Particle filters were located at the reactor gas entry port. The nominal chamber pressure was 26.7 kPa (200 torr) as measured with a capacitance manometer. The nominal susceptor rotation rate was 500 rpm. The reactor was mounted on a translation stage with three orthogonal axes of travel.

For elastic light scattering measurements, a laser sheet was formed by expanding a 488 nm wavelength beam with a ~25 mm focal length cylindrical lens and focusing the light into the reactor with a 500 mm focal length cylindrical lens.

*In situ* Raman spectra of gas phase nucleated particles were performed using the SiH4/N2/He gas mixture and as a function of thermocouple temperature. When detected, elastic light scattering due to particles was observed in a layer up to ca. 3 mm thick [6]. So, for a given temperature, the position of the maximum intensity of elastic laser light scattering was selected as the position for the Raman scattering measurement. The thermocouple temperature and the distance from the measurement position to the wafer surface are listed in Table 1. All spectra were recorded in the center of the reactor. The optical system has been previously described [5,6], and is summarized here for convenience. The spectra were excited with ca. 5 W of 488 nm radiation at the reactor tube. To reduce laser power density in the reactor (and thereby minimize potential laser-induced heating effects), a cylindrical lens was used. The resulting laser sheet was ca. 250 μm high by ca. 3 mm wide. The 3 mm plane was oriented parallel to the wafer surface to maximize vertical spatial resolution. Scattered radiation was collected at 90° to the direction of propagation of the exciting laser beam and collimated with an achromatic lens located at infinite conjugate ratio. A periscope, holographic notch filter, and a bandpass filter were placed in the collected, collimated radiation. The periscope consisted of two mirrors that served to rotate the image of the laser line so that the long axis of the image was parallel to the spectrograph slits. The bandpass filter was necessary to limit the amount of blackbody radiation entering the spectrograph so as to reduce interference from reentrant light. An achromatic lens was used to couple radiation into a 0.5 m focal length, f/6.5 aperture ratio imaging spectrograph equipped with an 1800 groove/mm grating blazed at 500 nm. A 2048 x 512 pixel array, back-illuminated, thermo-electrically cooled, charge coupled device (CCD) camera system was employed. The individual CCD pixel size was 13.5 μm x 13.5 μm. The sampling length in the reactor was ca. 3.2 mm (412 rows of the CCD array were used). The instrumental bandpass (FWHM) was ca. 2.4 cm⁻¹. All spectra were obtained in integration times of 5 min or less.

Gas phase temperatures were determined from the nitrogen rotational Raman spectra in the N2/He gas mixture. The experimental configuration is nominally identical to the configuration used for particle scattering measurements with a few exceptions. The beam was focused into the reactor with a 500 mm focal length spherical lens that produced a beam waist with a ca. 250 μm diameter (although the sampling length in the reactor was nominally identical to that employed for the particle Raman scattering measurements). A 2400 groove/mm holographic grating optimized for use from 450 nm to 750 nm was employed. The instrumental bandpass (FWHM) was ca. 2 cm⁻¹. Gas temperatures were determined by
comparing a measured Raman spectrum to a calculated spectrum and employing a global search minimization to minimize the sum of the residuals squared, as previously described [5,6]. Due to the sharp temperature gradients present in this reactor, and pending the results of a separate investigation in a reference isothermal gas cell, a thorough error analysis has yet to be performed. Therefore, reported rotational temperatures must be considered tentative. However, it has been reported that, depending on measurement conditions, rotational Raman spectroscopy can provide temperature measurements accurate to within ca. 2% to 5% [9,10].

TABLE 1. Thermocouple temperature and wafer-surface-to-measurement-position distance for Raman spectroscopic measurements of particles.

<table>
<thead>
<tr>
<th>Nominal Thermocouple Temperature (K)</th>
<th>Distance from Wafer Surface to Measurement Position (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>823 ± 10</td>
<td>3.00</td>
</tr>
<tr>
<td>873 ± 11</td>
<td>3.00</td>
</tr>
<tr>
<td>923 ± 11</td>
<td>3.00</td>
</tr>
<tr>
<td>973 ± 12</td>
<td>3.48</td>
</tr>
<tr>
<td>1023 ± 13</td>
<td>3.77</td>
</tr>
<tr>
<td>1073 ± 13</td>
<td>3.72</td>
</tr>
<tr>
<td>1100 ± 14</td>
<td>3.69</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

FIGURE 1. An image of the reactor with injection of the SiH$_4$/N$_2$/He gas mixture and a nominal thermocouple temperature of 1100 K.

Under the process conditions employed in this investigation, gas phase nucleated particles were detected by elastic laser light scattering for nominal susceptor temperatures of ca. 873 K and higher. Figure 1 shows an image of the reactor with injection of the SiH$_4$/N$_2$/He gas mixture and a nominal thermocouple temperature of 1100 K. A layer of particles is observed, the position and thickness of the layer varying with process conditions.

Figure 2 shows the in situ Raman spectra of the particle layer as a function of nominal thermocouple temperature, for all temperatures at which particle Raman scattering was observed. The peak at ca. 587 cm$^{-1}$ is attributed to molecular hydrogen (H$_2$) rotational Raman scattering. Hydrogen is a product of silane pyrolysis [6]. Hydrogen is not observed in the spectra recorded at temperatures above 1023 K because of interference from particle incandescence and Rayleigh scattering. This interference is the reason that the 1073 K and 1100 K spectra must be scaled for comparison in Fig. 2 (see Fig. 2 caption). The most intense features in each spectrum in Fig. 2 are due to the transverse optical (TO) phonon of $\alpha$-Si and/or $c$-Si, indicated by vertical dashed lines at 460 cm$^{-1}$ and 502 cm$^{-1}$, respectively. Depending on the temperature at which the spectrum was recorded, $\alpha$-Si and/or $c$-Si features are observed. The spectrum obtained at 923 K shows a single broad feature at ca. 460 cm$^{-1}$. The spectrum obtained at 973 K shows a relatively intense, broad $\alpha$-Si peak with a higher-wavenumber shoulder attributed to $c$-Si. The spectrum obtained at 1023 K shows a relatively intense $c$-Si peak with a lower-wavenumber shoulder attributed to $\alpha$-Si. The spectra obtained at 1073 K and 1100 K show relatively intense $c$-Si peaks. The $c$-Si peaks in these spectra exhibit low-wavenumber asymmetry. This asymmetry is attributed to signal originating from a remaining $\alpha$-Si or $\alpha$-Si-like component, possibly from surface modes at the grain boundaries [11]. Although no particle Raman scattering was observed at temperatures below 923 K, elastic laser light scattering signal was observed at 873 K. This result indicates that particles formed below 923 K but that Raman spectroscopy was insensitive to their presence, presumably because the concentration of particles was too low.

In Fig. 2, the $c$-Si TO phonon wavenumber is observed to shift from ca. 502 cm$^{-1}$ in the spectrum obtained at 1023 K to ca. 495 cm$^{-1}$ in the spectrum obtained at 1100 K. A red shift of the TO phonon wavenumber is expected: the gas temperature at the position of the Raman measurement is higher for a higher susceptor temperature and the $c$-Si TO phonon wavenumber is known to shift to lower wavenumber with increasing temperature [12]. However, the lowest expected $c$-Si TO phonon wavenumber for a temperature of 1100 K is ca. 501 cm$^{-1}$ [13]. Hence the cause of the observed ca. 7 cm$^{-1}$ red shift can not be attributed to thermal effects alone. Two other factors that could lead to a red shift of the $c$-Si TO phonon wavenumber are stress [14] and phonon-confinement
The magnitude of the expected Raman wavenumber shift for typically encountered values of stress is only ca. 0.1 % [14], too small to account for the entire observed red shift. Hence, some amount of phonon confinement is indicated by the magnitude of the shift observed in Fig. 2. Since phonon confinement effects are only observed for crystalline domain sizes in the ca. 3 nm to ca. 10 nm range, this indicates an approximate crystallite size range for the particles investigated in this work (although the crystallite size range may be smaller than the overall particle size). While the crystalline size range can be deduced from the Raman spectra, the degree of agglomeration cannot be determined from the spectra.

The spectra shown in Fig. 2 indicate an amorphous-to-crystalline silicon transition temperature above ca. 923 K and possibly near ca. 973 K. If one assumes that the presence of particles does not significantly perturb the rotational temperature profile, then the gas temperature at the measurement position can be determined from rotational Raman scattering measurements in the absence of particles. For small particles in a low-pressure ambient gas, the assumption that the presence of particles does not affect the gas temperature is probably reasonable [18]. However, this issue has yet to be investigated in this reactor. Figure 3 shows the measured rotational Raman temperature as a function of distance from the wafer surface for a nominal thermocouple temperature of 973 K. At distances from the wafer surface of ca. 12 mm and less, the change in temperature with distance from the susceptor is reasonably linear. The solid line is a linear regression fit to the data points indicated. This fit indicates a nominal y-intercept and slope of 1001 K and -38.7 K/mm, respectively. The particle Raman spectrum obtained at 973 K was measured 3.48 mm above the wafer surface (see Table 1). Based on the linear regression fit, the gas temperature at 3.48 mm was ca. 866 K. Assuming the same gas temperature in the presence of and absence of particles, this indicates that the amorphous-to-crystalline silicon transition occurs near ca. 866 K. This transition temperature is in good agreement with a reported transition temperature of ca. 848 K for low pressure CVD materials [17].

FIGURE 2. In situ Raman spectra of the particle layer as a function of nominal thermocouple temperature ($T_{TC}$). For comparison, the spectral intensity of the 1073 K and 1100 K spectra are divided by four (4) and five (5), respectively, and the spectra are offset on the vertical scale. The nominal Raman shift of $\alpha$-Si and c-Si are indicated by vertical dashed lines.

In Fig. 2, the $\alpha$-Si peak in the spectrum obtained at 923 K is observed at ca. 460 cm$^{-1}$. At room temperature, a peak at this wavenumber indicates $\alpha$-Si with no hydrogen incorporated into the material [15]. As mentioned above, temperature and stress effects make it difficult to draw definitive conclusions from this peak position. However, no Si-H stretching modes were observed in spectra (not shown) recorded in the ca. 1985 cm$^{-1}$ to ca. 2140 cm$^{-1}$ range [16], indicating low hydrogen content in these particles. A low hydrogen content at these particle growth temperatures is consistent with reports for low-hydrogen CVD $\alpha$-Si grown at similar temperatures [17].
CONCLUSIONS

In situ Raman spectra of gas phase nucleated particles were collected as a function of wafer surface temperature in a thermal CVD reactor. The Raman spectra showed that the particles were composed of α-Si and/or c-Si, depending on growth temperature. Raman spectral features of the c-Si also indicated crystalline domain sizes in the ca. 3 nm to ca. 10 nm size range. Gas phase temperature (in the absence of particles) was determined from nitrogen pure rotational Raman spectra and used to estimate an amorphous-to-crystalline silicon transition temperature of ca. 866 K for the gas phase nucleated particles.

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REFERENCES


13. Unpublished results (2003). This TO phonon wavenumber was measured on a c-Si wafer in this CVD reactor and with a nominal thermocouple temperature of 1100 K. It is unlikely that particles in the gas phase are at a higher temperature than the wafer surface.


