NRC Publications Archive Archives des publications du CNRC

Raman and transmission electron microscopy study of disordered silicon grown by molecular beam epitaxy

Tay, L.; Lockwood, D. J.; Baribeau, J. -M.; Wu, X.; Sproule, G. I.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1116/1.1676345>

Journal of Vacuum Science and Technology A, 22, 3, pp. 943-947, 2004

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=f2d5549f-6c55-4f41-a716-713f9f6e44e0>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=f2d5549f-6c55-4f41-a716-713f9f6e44e0>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research
Council Canada

Conseil national de
recherches Canada

Canada

Raman and transmission electron microscopy study of disordered silicon grown by molecular beam epitaxy

L. Tay,^{a)} D. J. Lockwood, J.-M. Baribeau, X. Wu, and G. I. Sproule

Institute for Microstructural Sciences, National Research Council Canada, Ottawa K1A 0R6, Canada

(Received 12 September 2003; accepted 20 January 2004; published 18 May 2004)

Silicon films were deposited by molecular beam epitaxy onto crystalline silicon (*c*-Si) and native oxide on *c*-Si (001) substrates at temperatures ranging from 98 to 572 °C. Raman spectroscopy of these films showed that both the short-range disorder and intermediate-range disorder decreases as the deposition temperature increases. The onset of a phase transition in the amorphous Si films can be effectively identified by the appearance of the polycrystalline and crystalline Si Raman bands, which allowed quantification of the crystalline volume fractions present. Both the transmission electron microscopy and Raman results confirmed that films grown on the amorphous substrates at temperatures less than 414 °C are entirely amorphous, but exhibit *c*-Si features at higher temperatures. Films grown on *c*-Si substrates exhibit a characteristic limiting thickness for epitaxy and the transformation of the resulting upper amorphous layer into crystalline form takes place at a much lower temperature (~290 °C) than for the amorphous substrates. © 2004 American Vacuum Society. [DOI: 10.1116/1.1676345]

I. INTRODUCTION

Silicon (Si) is the key material in the semiconductor industry. There have been many studies devoted to the thin film deposition of various phases of Si by techniques such as sputtering,¹ chemical vapor deposition (CVD),² and molecular beam epitaxy (MBE).³ The MBE technique, in particular, is performed in ultrahigh vacuum conditions and offers superior control over growth parameters such as temperature and growth rate. Thus, MBE is an interesting alternative to conventional techniques for the synthesis of a noncrystalline Si possessing fewer impurities and improved physical properties. The structural properties of low-temperature high-vacuum deposited Si have, until recently, not been the subject of much investigation. In particular, the degree of disorder in such Si films and its dependence on the processing temperature or nature of the substrate have not been fully examined. Earlier studies^{4–6} showed that the epitaxial growth of Si on a crystalline Si (*c*-Si) substrate at a given temperature is characterized by a limiting thickness (h_{epi}) beyond which the growth becomes amorphous. The structural evolution that leads to the epitaxy breakdown has not been studied in great detail and how the properties of those films compare to those of Si films deposited on noncrystalline substrates has also received little attention.

Raman spectroscopy is a nondestructive characterization technique sensitive to short and long-range atomic order. There have been a number of studies^{1,8} that have employed Raman scattering to characterize the phase transition of CVD grown silicon. It is a convenient method to study silicon phase transitions in amorphous silicon (*a*-Si),⁷ polycrystalline silicon (poly-Si),^{8,9} and *c*-Si materials.¹⁰ Despite its popularity, there have been few reports¹¹ of the use of Raman scattering spectroscopy to investigate the levels of disorder

and the phase transitions in low-temperature MBE-grown Si films. Here, we present a comprehensive Raman study of MBE-grown silicon films deposited on both crystalline and amorphous substrates and we compare the degree of film disorder as a function of the deposition temperature and the nature of the substrate. We show that there is a good agreement between the results obtained from Raman spectroscopy, secondary ion mass spectrometry (SIMS), and transmission electron microscopy (TEM) imaging.

II. EXPERIMENT

A number of samples were prepared by depositing Si on 100 mm Si (001) wafers in a VG Semicon V80 MBE system at a fixed growth rate of 0.2 nm/s. For the films grown on *c*-Si substrates, the Si wafers were treated in a 5% HF solution to remove the native oxide. The treatment left the wafer surface passivated with hydrogen, which was desorbed at 600 °C in the ultrahigh vacuum before Si deposition. A series of Si films were also deposited directly on Si (001) wafers that had received an UV-ozone treatment to reduce hydrocarbon surface contamination, but no HF treatment to remove the surface native oxide (SiO₂/*c*-Si). Films were deposited in the temperature range from 98 to 572 °C and were typically 350 nm thick.

Raman spectroscopy of each silicon film was performed in an ambient atmosphere of helium at room temperature (295 K). Samples were excited with 200 mW of 457.9 nm light from an Ar ion laser. The samples were investigated with a pseudo-backscattering geometry.¹² The scattered light was dispersed by a Spex 14018 double monochromator at a spectral resolution of 7.8 cm⁻¹ and detected with a cooled RCA C31034A photomultiplier tube. The incident light was polarized in the scattering plane and the scattered light was recorded without polarization analysis. In order to obtain the peak intensity, peak width, and integrated area of the various Si-related bands in the measured Raman spectra, a spectral

^{a)}Author to whom correspondence should be addressed; electronic mail: lilin.tay@nrc.gc.ca

TABLE I. Summary of the growth temperature, substrate, film thickness and crystalline volume fractions, X_c for the films that exhibit the *a*-Si, poly-Si, and *c*-Si Raman signatures.

Growth temp. (°C)	Substrate	Film thickness (nm)	X_c
295	<i>c</i> -Si	390	0.44
335	<i>c</i> -Si	316	0.88
374	<i>c</i> -Si	367	0.98
335	SiO ₂ / <i>c</i> -Si	370	0.009
414	SiO ₂ / <i>c</i> -Si	260	0.08
493	SiO ₂ / <i>c</i> -Si	400	0.97
572	SiO ₂ / <i>c</i> -Si	410	0.98

curve fitting was performed using a combined Gaussian–Lorentzian function. The structural properties of the Si thin films grown on both *c*-Si and SiO₂/*c*-Si substrates were also characterized by cross-sectional TEM to assess their microstructure and SIMS to probe their impurity incorporation. The TEM samples were examined with a Philips EM430T operating at 250 kV.

Due to the difference in the optical properties of *a*-Si, poly-Si, and *c*-Si, the Raman penetration depth for the 457.9 nm radiation varies for different types of films. The Raman penetration depth⁷ is ~ 19.2 nm for *a*-Si,⁷ ~ 321.6 nm for *c*-Si,¹² and somewhere in between for poly-Si. Referring to the film thicknesses shown in Table I, we are confident in concluding that there is very little, if any, Raman contribution from the *c*-Si substrate.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show TEM cross-sectional images of a Si film grown at 335 °C on a *c*-Si substrate and at 572 °C on a SiO₂/*c*-Si substrate, respectively. The concentric speckle-like halo rings in both selected area diffraction patterns suggest the presence of both *a*-Si and poly-Si. The film growth in Fig. 1(a) begins with ~ 75 nm of perfect crystalline growth followed by a breakdown of epitaxy characterized by the columnar defect structure along the [001] growth direction. This structure is very similar to that found for other MBE films deposited onto a crystalline substrate at low temperature.⁴ This type of growth evolution is, however, different from that for CVD or sputter deposited Si films, which tend to begin their phase transition through the random formation of pockets of *c*-Si grains within an *a*-Si network.^{13,14} Abundant twinning structures (planar defects) appear in the {111} planes at the interface where the epitaxial breakdown is observed. Such a twinning structure is commonly observed at the transitional state and acts as the strain relieving mechanism within the crystalline lattice network. On SiO₂/*c*-Si substrates, however, a polycrystalline structure with no definite depth dependence is observed. Dark striations in image (b) are mostly poly-Si with some *a*-Si embedded in the poly-Si. They appear to possess a columnar character rather than the stacking fault nature seen in image (a). The SIMS profile [see Fig. 1(c)] obtained from the same sample as in Fig. 1(a) shows a peak in the hydrogen concen-

FIG. 1. Cross-sectional TEM images and their corresponding selected area diffraction patterns (insets) of a Si film grown on (a) a *c*-Si substrate at 335 °C and (b) a SiO₂/*c*-Si substrate at 572 °C. The scale bar length is 100 nm. Part (c) is the hydrogen (solid line), oxygen (dotted line), and carbon (dashed line) secondary ion mass spectrometry profile of the Si film depicted in Fig. 1(a).

tration at the depth (denoted by the arrow) where the defects are first observed. This is consistent with H atoms segregating to the surface in the crystalline phase and being incorporated at the transition region. The oxygen and carbon incorporation remained low until the film crystallinity had strongly deteriorated.

The Raman spectrum of an *a*-Si epitaxial layer grown at 177 °C on a *c*-Si substrate is presented in Fig. 2. It is a characteristic *a*-Si Raman spectrum typified by the strong transverse optical (TO) and broad transverse acoustic (TA) phonon bands located at 475.8 and ~ 150 cm⁻¹, respectively. Less obvious longitudinal acoustic (LA) modes at 299.3 and 400.6 cm⁻¹ are visible, as shown by the deconvoluted (fitted) dashed traces in Fig. 2.

Figure 3 shows the Raman spectrum of the Si film depicted in Fig. 1(a), with the *c*-Si spectrum subtracted from it. The Raman spectrum still exhibits a noticeable TA band at 150 cm⁻¹. A much narrower band with a rather obvious

FIG. 2. Raman spectrum of an *a*-Si sample (solid trace) grown at 177 °C on a *c*-Si substrate. The deconvoluted TO and LA bands are represented by the dashed Gaussian-Lorentzian curves.

shoulder now replaces the broad TO band seen in the *a*-Si spectrum (see Fig. 2). The shoulder structure is a unique indicator of the presence of poly-Si or microcrystalline Si.⁸ Its asymmetric band shape differs markedly from the *c*-Si symmetric band at 520 cm⁻¹. The deconvoluted TO band comprises the *a*-Si related band at 481.2 cm⁻¹ and the poly-Si related bands at 505.5 and 517.3 cm⁻¹ (see the inset to Fig. 3). Depending on the amount of microcrystallinity present in the sample, the two higher frequency bands can vary in intensity. Correlating the Raman spectra in Fig. 3 with the TEM and diffraction results in Fig. 1(a), it is clear that this film is in a transitional stage at which all three phases of silicon (*a*-Si, poly-Si and *c*-Si) coexist. Therefore, the presence of crystalline (520 cm⁻¹) and microcrystalline Si (505, 517 cm⁻¹) bands in the Raman spectra offers an alternative way (in addition to TEM or x-ray diffraction) to characterize the onset of the phase transition in the MBE deposited Si films grown at various temperatures.

FIG. 3. Raman spectrum of a Si film (solid trace) grown at 335 °C on a *c*-Si substrate. Dashed curves represents the partially deconvoluted Raman spectra. Curve resolved TO bands are shown in the inset.

The integrated intensity of the crystalline components, I_c , normalized to the total scattering intensity in the TO band (including the *a*-Si component, I_a , near 480 cm⁻¹) is often used to determine the Si crystalline volume fraction present in the Raman sampled volume.^{8,15} The crystalline volume fraction evaluated by the formula,¹⁵ $X_c = I_c / (I_c + yI_a)$, where $y = 0.28$,¹⁶ is summarized in Table I. The weighting factor y is the ratio of the integrated Raman cross section for *c*-Si to *a*-Si at the excitation wavelength of 457.9 nm.¹⁶ Again, we stress the importance of the difference in the optical absorptions of the *a*-Si and *c*-Si at 457.9 nm, which is taken into account by the correction factor y in the X_c expression. It is important to point out that the X_c values listed in Table I are computed strictly for the volume of the film sampled by the Raman beam. For a Si film deposited on a *c*-Si substrate, the presence of poly-Si is first observed at growth temperatures higher than 295 °C. Although there is a thin crystalline epilayer (due to the limiting thickness issue) present in the samples grown below 295 °C, it is buried under a thick layer of *a*-Si and is not accessible with the 457.9 nm radiation used in the Raman sampling. As the growth temperature increases, the crystalline volume fraction increases from 0.44 (at 295 °C) to 0.98 (at 374 °C). The films grown on *c*-Si at the next temperature of 414 °C or higher produced an entirely *c*-Si-like Raman signature. Poly-Si Raman features were first observed at a higher temperature (335 °C) for films grown on SiO₂/*c*-Si (see Table I). It is interesting to point out that high crystalline volume fractions could be observed in Si films even though they were grown on noncrystalline substrates. This suggests a high degree of crystallinity is achievable on noncrystalline substrates provided that the deposition temperature is high enough.

At low temperature, Si growth on *c*-Si substrates is initially epitaxial up to a critical thickness beyond which the crystalline growth gives way to amorphous growth. The TEM images in Fig. 1(a) show the evolution of the Si film grown at 335 °C on a *c*-Si substrate. The growth is epitaxial over the first ~75 nm deposited above the *c*-Si substrate; it evolves into a poly-Si intermediate layer in the next 200 nm and then finally into a 50-nm-thick layer *a*-Si near the surface. However, films deposited on native oxide SiO₂/*c*-Si have no crystalline template to conform to and grow directly in an amorphous phase and the transition from *a*-Si to poly-Si occurs at a much higher temperature. Raman spectra of films grown on amorphous substrates suggest the poly-Si phase does not appear below ~500 °C. The growth of poly-Si phases on amorphous substrates had a columnar form and was embedded within an *a*-Si matrix.

The inelastically scattered light signals arise from the lattice vibrations in solids. The various bands observed in the Raman spectrum thus reflect the vibrational density of states of either the optical or acoustic phonons in the solid structure. The TO-like phonon is due to vibrations associated with bonding between nearest neighbor atoms. It is well established that an increase of the linewidth, Γ (defined as the full width at half maximum), and a decrease of the peak frequency, ω_{TO} , of the TO band are related to the root-mean-

FIG. 4. Linewidth, Γ , of the TO band is plotted as a function of the film growth temperature for the two different substrates.

square bond-angle distortion (short-range disorder) in a disordered Si network.^{17,18} The peak broadening is due to the random distribution of the internal strain.¹⁸ The relationship between Γ and bond-angle distortion (from the *c*-Si value of 109.5°) $\Delta\theta$ has been established by Beeman, Tsu, and Thorpe who found that $\Gamma = 15 + 6\Delta\theta$.¹⁷ Figure 4 shows a clear trend of decreasing Γ and hence $\Delta\theta$ as the deposition temperature increases. At the lowest growth temperature (98°C) on the amorphous substrate, the Γ value of 71.8 cm^{-1} corresponds to a bond-angle distortion of 9.47° . For *a*-Si films grown on a *c*-Si substrate, the experimentally observed Γ values ranged from 72.8 to 61.0 cm^{-1} implying bond distortion angles in the range of 9.63° to 7.67° for films grown in the temperature range of 177 to 374°C . Beeman and co-workers¹⁷ reported a $\Delta\theta$ ranging from 7.7° to 10.5° for MBE films grown at 33°C and annealed up to 600°C . The respective $\Delta\theta$ values are in good agreement. The slightly higher $\Delta\theta$ found by Beeman and co-workers is due to the lower deposition temperature of 33°C . The decrease in $\Delta\theta$ implies that the deposited film becomes more ordered with increasing deposition temperature. However, Γ for the *c*-Si substrate case (solid square, Fig. 4) showed a slight increase at the highest growth temperature where poly-Si or *a*-Si is formed (374°C). A similar effect has been observed in glow discharge and sputter deposited Si films.¹⁹ This is due to the contributions from two opposing factors. As the temperature increases, the higher mobility of Si atoms improves the network relaxation. On the other hand, hydrogen dissociation at higher temperature removes its strain relieving effect from the Si network.¹⁹ Results from SIMS confirmed a much lower level of H content in the film grown at 374°C or above.²⁰

As the growth temperature increases, an increasing trend from 477.3 cm^{-1} at 98°C to 490.6 cm^{-1} at 493°C for ω_{TO} also indicates diminishing disorder in the deposited films. At the highest deposition temperature of 572°C , we found that the film grown on $\text{SiO}_2/\text{c-Si}$ shows a relatively lower ω_{TO} value. This change corresponds to the onset of the formation of poly-Si and an abrupt change in the short-range order

within the epilayer. The results overall agree well with the cross-sectional TEM study.

In contrast to the TO mode, the TA mode is associated with vibrations of disordered structures that extend beyond the immediate neighboring atoms, of the order of $4\text{--}6\text{ \AA}$ or greater.²¹ Thus the TA peak intensity in Raman spectra is a good indication of the intermediate range disorder. To exclude the possibility of contributions from sample to sample intensity variations due to changes in optical absorption, the intensity ratio of the TA peak to TO peak, $I_{\text{TA}}/I_{\text{TO}}$, is taken as the measure of intermediate range disorder for the *a*-Si network. Hence, a decrease in the intermediate-range order is manifested in an increase of the intensity ratio of the TA and TO bands. This trend is most evident in films grown on $\text{SiO}_2/\text{c-Si}$. As the growth temperature of the *a*-Si film increases, the $I_{\text{TA}}/I_{\text{TO}}$ ratio shows a general decreasing trend from 0.67 at 98°C to 0.22 at 572°C , indicating an increase of intermediate-range order. In the case of *c*-Si substrates, we observed a sudden increase in the band ratio at 295°C . This, again, shows a connection to the onset of a phase transition from *a*-Si into poly-Si and hence an abrupt change in the intermediate-range disorder.

IV. CONCLUSION

We have presented detailed Raman characterization results for MBE-grown Si films deposited on *c*-Si (001) and $\text{SiO}_2/\text{c-Si}$ (001) at various growth temperatures. The observed decrease in the TO phonon bandwidth and increase in the peak frequency as the growth temperature increases indicate an increased short-range order within the film network. In addition, the decrease in the TA-to-TO band intensity ratio indicates an increase in the intermediate-range order as the film growth temperature increases. We have also shown that the onset of the phase transition from *a*-Si into poly-Si and *c*-Si films can be easily characterized by the appearance of the related Raman bands near 505 and 517 and 520 cm^{-1} , respectively. We have determined the volume fraction, X_c , of the crystalline phase in the films deposited onto the different substrates and it rises steeply at first with increasing growth temperature. Finally, we have demonstrated that Raman spectroscopy is a convenient and effective way to study the degree of disorder and to identify the phase transition in MBE-grown silicon films.

¹K. Xu, S. I. Shah, and D. Guerin, J. Vac. Sci. Technol. A **19**, 1078 (2001).

²D. Han, G. Yue, J. D. Lorentzen, J. Lin, H. Habuchi, and Q. Wang, J. Appl. Phys. **87**, 1882 (2000).

³D. J. Eaglesham, J. Appl. Phys. **77**, 3597 (1995).

⁴D. J. Eaglesham, H. J. Gossman, and M. Cerullo, Phys. Rev. Lett. **65**, 1227 (1990).

⁵D. J. Eaglesham, J. Appl. Phys. **62**, 2566 (1993).

⁶J. Thiesen, H. M. Branz, and R. S. Crandall, Appl. Phys. Lett. **77**, 3589 (2000).

⁷P. X. Zhang, I. V. Mitchell, B. Y. Tong, P. J. Schultz, and D. J. Lockwood, Phys. Rev. B **50**, 17080 (1994).

⁸M. Zhu, X. Guo, G. Chen, H. Han, M. He, and K. Sun, Thin Solid Films **360**, 205 (2000).

⁹Z. Iqbal, S. Veprek, A. P. Webb, and P. Capezzuto, Solid State Commun. **37**, 993 (1981).

¹⁰P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors*, 2nd ed. (Springer, Berlin, 1999).

- ¹¹D. J. Lockwood, J.-M. Baribeau, M. Noel, J. C. Zwinkels, B. J. Fogal, and S. K. O'Leary, *Mater. Res. Soc. Symp. Proc.* **609**, A5.1.1 (2000); D. J. Lockwood, J.-M. Baribeau, M. Noel, J. C. Zwinkels, B. J. Fogal, F. Orapunt, and S. K. O'Leary, *ibid.* **715**, A19.1.1 (2002).
- ¹²D. J. Lockwood, M. W. C. Dharma-Wardana, J. M. Baribeau, and D. C. Houghton, *Phys. Rev. B* **35**, 2243 (1987).
- ¹³A. Lambertz, B. S. Richards, A. B. Sproul, T. Puzzer, and M. Gross, *Proceedings of the Second World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, Vienna, Austria, 6–10 July (1998), VB1.22.
- ¹⁴T. Sasaki, S. Fujikake, K. Tabuchi, T. Yoshida, T. Hama, H. Sakai, and Y. Ichikawa, *J. Non-Cryst. Solids* **266–269**, 171 (2000).
- ¹⁵R. Tsu, J. Gonzales-Hernandez, S. S. Chu, S. C. Lee, and K. Tanaka, *Appl. Phys. Lett.* **40**, 534 (1982).
- ¹⁶From Ref. 15, $y = (I_c / \alpha_c) / (I_a / \alpha_a)$ where α is the absorption coefficient for crystalline and amorphous Si at the excitation wavelength of 457.9 nm. Using $\alpha_c = 3.58 \times 10^4 / \text{cm}^{-1}$ obtained from Ref. 12 and $\alpha_a = 6.0 \times 10^5 / \text{cm}^{-1}$ obtained from Ref. 7, and $I_c / I_a = 4.70$ determined experimentally, y is calculated to be 0.28 for 457.9 nm excitation.
- ¹⁷D. Beeman, R. Tsu, and M. F. Thorpe, *Phys. Rev. B* **32**, 874 (1985).
- ¹⁸R. Tsu, J. Gonzalez-Hernandez, and F. H. Pollak, *Solid State Commun.* **54**, 447 (1985).
- ¹⁹G. Morell, R. S. Katiyar, S. Z. Weisz, H. Jia, J. Shinar, and I. Balberg, *J. Appl. Phys.* **78**, 5120 (1995).
- ²⁰J. M. Baribeau, X. Wu, D. J. Lockwood, L. Tay, and G. I. Sproule, *J. Vac. Sci. Technol.* (in press).
- ²¹A. P. Sokolov, A. P. Shebanin, O. A. Golikova, and M. M. Mezdrogina, *J. Phys. Condens. Matter* **3**, 9887 (1991).