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Low-temperature Si growth on Si (001): Impurity incorporation and limiting thickness for epitaxy

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We present a structural and chemical analysis of high-vacuum deposited Si films grown on clean or oxidized Si (001) wafers by low-temperature molecular-beam epitaxy. For growth on clean Si, we observed a limiting thickness for epitaxy that decreases with decreasing temperature with an activation energy of 0.47 eV. The onset of defect formation is correlated to a peak in the H impurity concentration. The transition to an amorphous phase is, however, observed beyond the depth where impurities are first observed pointing to surface disorder/roughening as a source of epitaxy breakdown. The O and C content in these films remains low until the film crystallinity has strongly deteriorated and reaches a saturation concentration of 2–4 at. % in the fully amorphous regions. The impurity profiles in amorphous-Si films grown on oxidized Si are similar to those obtained on clean Si when grown at the same temperature and indicate that the impurity uptake depends primarily on residual gas and surface condition. Raman scattering results show the structural changes and evolution of the Si bond configuration. © 2004 American Vacuum Society.

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I. INTRODUCTION

There is interest in performing epitaxy at increasingly lower temperatures. For example, low-temperature processing can improve the interfacial abruptness and strain stability in heterostructures and prevent surface segregation or dopant diffusion. Structural studies of epitaxial Si grown at a low temperature on Si (001) have revealed the existence of a limiting thickness for epitaxial growth h for that system.^{1,2} As the temperature decreases, breakdown of epitaxy is observed at increasingly smaller thicknesses. Although the temperature dependence of h has been studied by several authors,^{1,3–5} the mechanism that leads to epitaxy breakdown is not fully understood and the concomitant impurity incorporation has not been investigated in detail. Surface hydrogen is known to exert a strong influence on Si growth and may be a catalyst to epitaxy breakdown by altering surface processes. An earlier review⁶ concluded that surface roughening, rather than chemical contamination, was more likely at the origin of the epitaxy breakdown. In a recent model,⁷ the crystalline-to-amorphous phase transition was linked to the supersaturation of the growing layer by hydrogen. A recent study⁸ of Ge (001) homoepitaxy shows that the epitaxial breakdown for that system is not controlled by hydrogen adsorption or an accumulation of defects, but rather by a growth mode transition driven by kinetic roughening.

Besides epitaxy breakdown, low-temperature Si deposition is also likely to result in greater impurity incorporation that can hinder the usefulness of such thin films. The impurity profiles in physical vapor deposited Si is also expected to differ from that found in more conventional amorphous-Si (a -Si) films produced by techniques such as chemical vapor

deposition or sputtering. It is thus of technological importance to probe the impurity profiles of such films.

Here, we report a study of the structural evolution and impurity incorporation in low-temperature Si molecular-beam epitaxy (MBE). The microstructural properties of Si films deposited at a low temperature on clean or oxidized Si (001) are studied by transmission electron microscopy (TEM) and Raman scattering spectroscopy, and the impurity profile is probed by secondary ion mass spectrometry (SIMS).

II. EXPERIMENT

A number of wafers were prepared by depositing Si on 100 mm Si (001) wafers in a Vacuum Generator Semicon V80 MBE system. The growth rate was fixed at 0.2 nm/s (except for one sample grown at 0.1 nm/s) and the temperature varied in the range of 98–414 °C. The wafer temperature was measured using a thermocouple calibrated against the melting points of In, Sn, and Pb. The Si wafer preparation consisted of a dilute HF dip to remove the native oxide and to leave a H-passivating layer that was desorbed in an ultrahigh vacuum at 600 °C prior to growth. A set of samples was also prepared under similar growth conditions by depositing Si directly on substrates that had not received the above-surface preparation, but only an ultraviolet ozone treatment leaving the surface covered with a hydrocarbon-free native oxide.

The various samples were examined in $\langle 110 \rangle$ cross-sectional TEM in a Philips EM430 operated at 250 kV. Hydrogen, carbon, and oxygen were analyzed by SIMS using a PHI Adept 1010 system with a 3 keV Cs-ion beam 60° off normal and a system background pressure of 4×10^{-11} Torr. Implant standards were used to calibrate the concentration of each element. The oxygen and carbon background levels in the wafers were also measured by glow

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FIG. 1. (Top) Cross-sectional TEM view of a Si film deposited on *c*-Si at a temperature of 374 °C with corresponding selected area diffraction pattern shown in inset, and (bottom) corresponding H, C, and O impurity profiles as measured by SIMS.

discharge mass spectrometry and were found to be consistent with the secondary ion mass spectrometer calibration. The Raman spectra were measured at 295 K. Samples immersed in He gas were excited in a pseudobackscattering geometry with 200 mW of 457.9 nm light from an Ar-ion laser.⁹ 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 Radio Corporation of America C31034A photomultiplier. The incident light was polarized in the scattering plane and the scattered light was recorded without polarization analysis.

III. RESULTS

A. Growth on crystalline silicon

Figure 1 shows a $\langle 110 \rangle$ cross-sectional TEM image of a sample grown at 374 °C and the corresponding SIMS profile.

The TEM image is shown sideways and scaled so that a one-to-one correspondence exists between the SIMS and TEM depth scales. Selected area diffraction (see inset, Fig. 1) in the epilayer region reveals the presence of twinned crystalline silicon (*c*-Si), microcrystalline Si (μc -Si) and *a*-Si. At the depth at which structural defects are first observed, the SIMS depth profile exhibits a peak in the H concentration. These first defects are stringlike features extending along the growth direction and are most likely linear arrays of microvoids.¹⁰ At that depth, there is no significant O or C uptake. These impurities start to build up exponentially only at a depth at which a significant fraction of the sample is heavily defected or microcrystalline. For this particular sample, the impurity decay length is ~ 35 nm. The vertical bar labeled *h* in Fig. 1 indicates the limit of epitaxial layer growth defined as the depth at which 50% of the film is nonepitaxial. This particular sample is not thick enough to observe a full transition to the amorphous phase near the surface.

Results qualitatively similar to those of Fig. 1 were obtained on all of the Si films deposited on *c*-Si. The solid lines in Fig. 2 present SIMS depth profiles for samples grown on *c*-Si at three different temperatures. For growth at lower temperatures, defects are observed much closer to the original interface and the transition region toward amorphous growth is much thinner. An exponential impurity build up with a characteristic decay length of between 15 and 50 nm takes place in the heavily defected transition region between *c*-Si (close to the substrate interface) and *a*-Si (near the surface). The O and H concentrations reach a saturation value of $\sim 1-2 \times 10^{21}$ cm⁻³ or $\sim 2-4$ at. % in the upper amorphous region. The oxygen and hydrogen profiles show identical fluctuations in the *a*-Si region, consistent with water adsorption. The periodic oscillations in the impurity concentration at the lowest temperature are due to power cycling of the substrate heater, which indicates that, besides the Si source electron gun, outgasing of the manipulator is a significant source of contamination in our experiment. At high growth temperatures (>300 °C), the C level follows a trend similar to the other impurities but, at any given depth, is typically one order of magnitude lower than O and H (see also Fig. 1). At decreasing temperatures below 300 °C, the C contamination is progressively reduced to reach levels in the mid- 10^{17} cm⁻³ below 200 °C. Note that above 400 °C, there is evidence of H incorporation in the film well before epitaxy breakdown as shown in Fig. 2(c).

Although the effect of the growth rate was not studied systematically here, the microstructure and impurity profile of a Si film grown at 335 °C at a rate of 0.1 nm/s was investigated. From TEM and Raman scattering spectroscopy, this sample has retained good crystallinity over a thickness of over 200 nm, or more than twice the value of *h* determined on the sample grown at the same temperature and at a rate of 0.2 nm/s. The impurity levels were also lower at the slower rate and their depth profile showed good similarity with films deposited at a higher temperature of 414 °C and the 0.2 nm/s rate.

FIG. 2. Impurity profiles for three Si films deposited on *c*-Si at the temperatures indicated (full lines). The vertical line corresponds to the depth of epitaxy breakdown as measured by transmission electron microscope cross-section imaging. The broken lines are impurity profiles for films deposited on oxidized Si under identical experimental conditions.

The variation of h with temperature is shown in Fig. 3 and compared to earlier results. The measured temperature dependence of h agrees well with most published data and can be fitted by an Arrhenius relationship with an activation energy of 0.47 ± 0.05 eV and pre-exponential factor of 1.27×10^{-3} m. At all temperatures, the onset of defect formation is correlated with a peak in the H concentration (see Fig. 2). Interestingly, the integrated H dose in that peak also obeys a similar Arrhenius relationship with activation energy of ~ 0.49 eV (see inset, Fig. 3) close to the extrapolated value for H diffusion in bulk *c*-Si in this temperature range.¹¹

Figure 4(b) shows a representative Raman result for Si films grown on *c*-Si. The spectrum is dominated by the broad transverse acoustic (TA) band at ~ 150 cm^{-1} and transverse optic (TO) band at ~ 480 cm^{-1} together with a sharp side band at 518.0 cm^{-1} . The less pronounced longitudinal acoustic modes at 302 and 416 cm^{-1} are shown by the deconvoluted dashed traces in Fig. 4(b). In the deconvolution, the broad TA band is represented by four Gaussian-Lorentzian curves and the complex TO structure is represented by the *a*-Si related Raman component at 479.0 cm^{-1}

FIG. 3. Limiting thickness for epitaxy h for Si deposition on Si (001). The inset shows the integrated dose in the hydrogen peak seen in SIMS depth profiles.

and μ c-Si related bands at 506.9 and 518.0 cm^{-1} . The relative intensity of the *a*-Si and μ c-Si bands varies as the growth temperature changes. At a higher growth temperature, the observed spectrum is similar to the one shown in Fig. 4(a), where the μ c-Si band (518.8 cm^{-1}) dominates the spectrum as the deposited film becomes more *c*-Si like. At the growth temperature of 414 $^{\circ}\text{C}$ and higher, the observed spectrum showed one single sharp peak at 520.0 cm^{-1} , im-

FIG. 4. Raman spectrum of a Si film deposited on (a) SiO_2 /*c*-Si at a temperature of 493 $^{\circ}\text{C}$ and (b) *c*-Si at a temperature of 295 $^{\circ}\text{C}$. The deconvoluted bands are shown by dashed curves. The inset in (b) shows the temperature dependence of the *a*-Si film TO-mode frequency for *c*-Si (open circles) and SiO_2 /*c*-Si (solid squares) substrates.

Fig. 5. (Left-hand side) Cross-sectional TEM view of a Si film deposited on the native oxide on a Si (001) wafer. Selected area diffraction (inset) and high-resolution lattice imaging (right-hand side) reveal the presence of a microcrystalline region in the sample.

plying that the film is comprised of *c*-Si. For films grown at 256 °C and lower, both μc -Si related bands were unobservable and the *a*-Si related TO structure dominates the spectrum. This is consistent with the deposited film taking on a completely *a*-Si-like character at a low growth temperature.

B. Growth on SiO₂/crystalline silicon

Due to the absence of a crystalline template, Si grows in an amorphous phase when deposited directly on an oxidized Si surface at a temperature below 500 °C. Above 500 °C, cross-sectional TEM and selected-area diffraction reveal a columnar morphology with the coexistence of microcrystalline and amorphous materials, as illustrated in Fig. 5.

Figure 4(a) shows Raman results for the Si film grown at 493 °C on SiO₂/*c*-Si. Again, the deconvolution (dashed curves) resolves the sharp TO band plus shoulder into the *a*-Si band at 490.6 cm⁻¹ and the μc -Si bands at 505.1 and 518.8 cm⁻¹. Similar to the film growth on *c*-Si, at a low growth temperature the spectrum is dominated by *a*-Si bands. These features eventually give way to the μc -Si bands as the crystallinity of the deposited film increases at a higher temperature. Unlike the single *c*-Si spectral features observed in films grown at a high temperature on *c*-Si, the films grown on SiO₂/*c*-Si still exhibit *a*-Si and μc -Si spectral features even at the highest growth temperature of 572 °C.

For the whole temperature range investigated, we observe that the contamination profiles at a given temperature do not depend much on whether Si is deposited epitaxially or in an amorphous state. This is illustrated in Fig. 2 where impurity profiles for films deposited on oxidized Si are shown in dotted lines. Apart from the expected impurity accumulation at the original oxidized interface, there is a striking qualitative similarity in the contamination profiles. While similar saturation levels near the surface are not surprising as they reflect the Si flux to impurity flux ratio, the similarity found deeper in the film is an interesting observation that indicates an

impurity uptake in the *a*-Si phase more characteristic of defective *c*-Si than bulk *a*-Si. This suggests that the impurity incorporation is primarily determined by the relative flux of Si and contaminant atoms impinging on the surface during growth and not the film crystallinity.

IV. DISCUSSION

Although there is a correlation between the H content and the onset of defect formation, the results presented here do not clearly link H to the phase transition in low-temperature deposited Si. The impurity profiles at a high temperature (414 °C) for example, show that some H is incorporated in the film well before the transition to the amorphous phase occurs. In fact, saturation of surface bonds by hydrogen does not by itself preclude epitaxial growth if Si—H atomic exchange is energetically favorable.⁶ There are also reasons to question the justification of linking the Arrhenius energy in Fig. 3 to the activation energy for H diffusion in *c*-Si. The latter has not been measured experimentally in the temperature range of MBE and the value of 0.48 eV generally quoted is based on an extrapolation from room-temperature data. The fact that the activation energy for *h* is dependent on the surface orientation¹² points to a critical surface process as the driving force in epitaxy breakdown. The observation of a larger limiting thickness and lower impurity concentration in a film grown at a lower rate as compared with a film grown at the same temperature at the usual rate, also indicates that the build up of surface disorder is conducive to the breakdown of epitaxy and enhanced impurity uptake.

The onset of the phase transition from *a*-Si into μc -Si and *c*-Si films can be easily characterized by the appearance of the related Raman bands near 505 and 517 cm⁻¹ and 520 cm⁻¹, respectively. The observed decrease of the TO phonon bandwidth, and increase of peak frequency [shown in the inset of Fig. 4(b)], as the growth temperature increases indicate an increased short-range order within the film network. At the highest deposition temperature of 572 °C, the film grown on SiO₂/*c*-Si shows a relatively lower TO peak frequency. This change corresponds to the onset of the formation of μc -Si and an abrupt change in the short-range order within the epilayer. The change in short-range order can be quantified by the bond angle distortion, $\Delta\theta$, from the *c*-Si value of 109.5°. The distortion is related to the TO bandwidth Γ , by the linear relationship $\Gamma = 15 + 6\Delta\theta$.¹³ For *a*-Si films grown in the temperature range of 177 to 374 °C on *c*-Si, the observed bond angle distortion ranges from 9.64° to 7.66°; for films grown in the temperature range from 98 to 572 °C on SiO₂/*c*-Si, the deviation in the bond angle ranges from 9.47° to 7.62°.

In addition, the decrease of TA to TO band integrated intensity ratio (I_{TA}/I_{TO}) indicates the increase of intermediate-range order as the film growth temperature increases. This trend is most evident in films grown on SiO₂/*c*-Si. As the growth temperature increases, I_{TA}/I_{TO} shows a general decreasing trend from 0.67 at 98 °C to 0.22 at 572 °C, indicating an increase of intermediate-range order.

The integrated intensity of the crystalline components normalized to the total scattering intensity in the TO band (including the *a*-Si component) is used to determine the Si crystalline volume fraction,¹⁴ X_c , present in the Raman sampling volume. The volume fraction, X_c , of the crystalline phase in the films deposited onto the different substrates rises steeply at first with increasing growth temperature. For example, an X_c value of 0.08 was observed for films grown on SiO₂/*c*-Si at 414 °C. This value increased to 0.97 and 0.98 for the samples grown at the two subsequent temperatures of 493 and 572 °C. Similar trends were observed for films grown on *c*-Si. At a temperature of 414 °C or above, the lack of an *a*-Si component in the Raman spectra indicates that the X_c is extremely close to 1. This observation suggests that, regardless of the substrate type, films grown at a very high temperature have the tendency of forming a high fraction of *c*-Si.

V. CONCLUSION

Although a correlation is found between the onset of defect formation and an increase in hydrogen incorporation in low-temperature Si homoepitaxy, the transition to the amorphous phase shows no clear link to a hydrogen surface saturation. Impurity levels in Si films grown on *c*-Si or SiO₂/*c*-Si exhibit a close similarity for any given process temperature. This suggests that impurity uptake does not play a major role in epitaxy breakdown, which more likely arises from morphological changes at the growth front. The impurity levels in *a*-Si obtained by vacuum deposition in a clean MBE environment are relatively low when compared

to *a*-Si grown by more conventional techniques. These films also exhibit unusual optical absorption properties¹⁵ and in the context of Si photonics may warrant further investigation.

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