X-ray Analysis of Si/Ge/Si(001) Heterolayer Structures Grown by Surfactant Mediated Epitaxy.

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ABSTRACT

X-ray diffraction and x-ray standing waves (XSW) have been used to investigate the quality of epitaxial ultra-thin Ge films grown on Si(001) with and without Te as a surfactant. The efficacy of Te as a surfactant in this application has been debated. We measured samples between 1 and 10 ML in thickness and our results clearly indicate that Ge films grown with Te are superior to those grown without Te. The coherent positions and coherent fractions determined from XSW analysis agree well with those predicted by linear elasticity theory for Ge/Si(001). Furthermore, grazing incidence diffraction measurements (GIXD) suggests that 9 ML Ge grown on Si(001) with Te is strained in-plane while the same film grown without Te is relaxed.

INTRODUCTION

The use of surfactants in Ge/Si(001) epitaxy has been studied in moderate detail. Surfactants act to improve epitaxial growth by decreasing the adatom (in our case Ge) surface mobility and, therefore, promote 2-D epitaxial growth. A prerequisite for a surfactant is to lower surface free energy, therefore, providing a driving force for the surfactant atom to site exchange with Ge adatoms as Ge is deposited. In addition to this, the surfactant should have a low solubility in both Si and Ge. Most work has focused on group IV elements (As[1], Sb[1,2]), however group IV and VI elements have also been investigated. In this work we have chosen Te to be used as the surfactant and have studied Ge films between 1 and 10 ML grown with and without a surfactant.

Te is a group VI element and is thus able to saturate the Si(001)[3] or Ge(001)[4] surface dangling bonds and create a truly passivated surface. Its solubility in both Si and Ge is also very low, therefore, reducing the likely-hood of any background doping in Si or Ge. RHEED[5,6] studies of the use of Te as a surfactant suggest that Te suppresses the extent of islanding by reporting streaked patterns up to 550 Å in thickness suggesting 2-D epitaxial growth. Additionally, cross-sectional TEM[5] of these same samples show the presence of stacking faults and two-phase diffraction patterns (Si and Ge) which suggest a variation of lattice parameter throughout the Ge film. Our x-ray studies have focused on the initial growth (>20 Å) of Ge on Si(001). By using high-resolution x-ray standing waves we were able to determine the registry of Ge adatoms with respect to the Si(001) bulk substrate lattice and conclude that Te as a surfactant acts to substantially decreases the amount of disorder in Ge epitaxial layers. Diffraction measurements in the vicinity of the in-plane 220 Bragg-peaks suggest that at 9ML Ge films are almost completely relaxed when grown without surfactant whereby they are pseudomorphic when grown with Te as a surfactant.

EXPERIMENT

The Si/Ge/Si(001) films were grown by molecular beam epitaxy in a UHV system with a base pressure lower than $1x10^{-10}$ Torr. The Si substrates were cleaned by the Shiraki Method and out-gassed overnight for at least 12 hours at 650°C. The samples were then flash annealed to 850°C until a sharp 2-domain 2x1 LEED pattern was observed. Ge was evaporated from a Knudsen cell at a rate of 0.1ML/min with the substrate held at 410°C. For the samples w/ Te, Te was deposited first onto a substrate held at 300°C and then annealed to 400°C for 10 minutes until a 1x1 LEED pattern formed. This 1x1Te:Si(001) surface reconstruction is understood to consist of ~ 0.8 ML of Te atoms residing on Si bridge sites with occasional Te missing rows to relieve the stress due to the significant size difference between Te and Si atoms[7]. A Te overpressure was maintained during both Ge and Si growth in order to compensate for possible Te desorption. The Si Cap was deposited from an e-beam evaporator operating at 110W with a corresponding growth rate of 1ML/min. The Ge coverage was verified by comparing its fluorescence signal to that of an ion-implanted standard and the Si cap thickness was determined by low-angle x-ray reflectivity.

The XSW scans were made at the NSLS X15A beamline. The measurements were made by monitoring the Ge K florescence signal while scanning in energy through either the Si(004) or Si(022) rocking curves. The coherent fraction and coherent position of the atoms in the Ge film with respect to the Si lattice was then determined by applying dynamical diffraction theory analysis to the data. A more detailed review of the XSW technique is available elsewhere [8]. The grazing incidence diffraction measurements (GIXD) were made on these samples using both synchrotron and "in-house" x-ray facilities. In this experiment the angle of incidence was kept at angles near the critical angle (~0.2°) for total external reflection from Si. By varying this angle slightly we were able to selectively probe different depths within the heterolayer.

RESULTS

The output parameters in our XSW measurement are coherent fraction (f_H) and coherent position (P_H). These are respectively the amplitude and phase of the *hkl* Fourier component of the atomic distribution function (F_{hkl})of all the atoms contributing to the fluorescence signal. Figure 1 compares florescence fits for two of the samples with and without surfactant. The stronger modulation (higher coherent fraction) in Ge florescence for sample (a) is characteristic of a higher degree of ordering in the epitaxy. Notice that this sample has a larger germanium coverage yet has a higher coherent fraction than sample (b). According to linear elasticity, the Ge coherent fraction is expected to drop as coverage increases (for 2.65 ML Ge/Si $f_{004}^{ideal} = 0.89$ and for 3.4 ML Ge/Si $f_{004}^{ideal} = 0.85$). This point will be addressed further in the following section.

For our grazing incidence diffraction measurements we were interested in comparing the in-plane lattice parameter of our samples. Figure 2 shows in-plane HK-scans at L = 0.03 for three different samples. (Each had a 65 Å thick Si cap.) At this grazing incidence condition the scattering depth is ca. 750 Å and thus the in-plane scattering is sensitive to the structure of the Si cap and Ge buried layer. For the 9 ML sample grown without a surfactant a peak is present at H = 1.93. This is close to the expected H = 1.92 position for a pure Ge bulk lattice constant,

implying that there exists relaxed Ge in the heterostructure. The 9 ML sample that was grown with Te as a surfactant shows no feature at this H value and, thus indicating that the Ge epilayer is strained with an in-plane lattice constant constrained to that of Si(001).

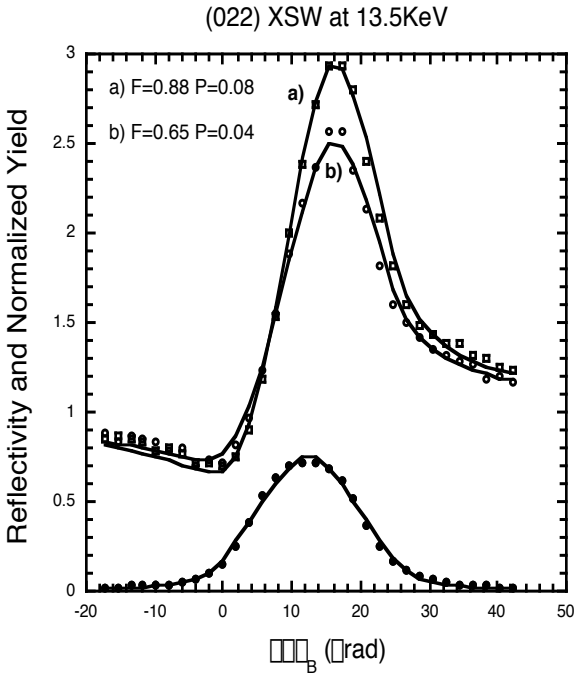

Figure 1. The experimental and theoretical angular dependency of the Ge K□ fluorescence yield and reflectivity collected while scanning in energy through the Si(022) Bragg reflection. Sample (a) is a 3.4 Ge ML film grown with Te as a surfactant while sample (b) is a 2.65 ML film grown with no surfactant.

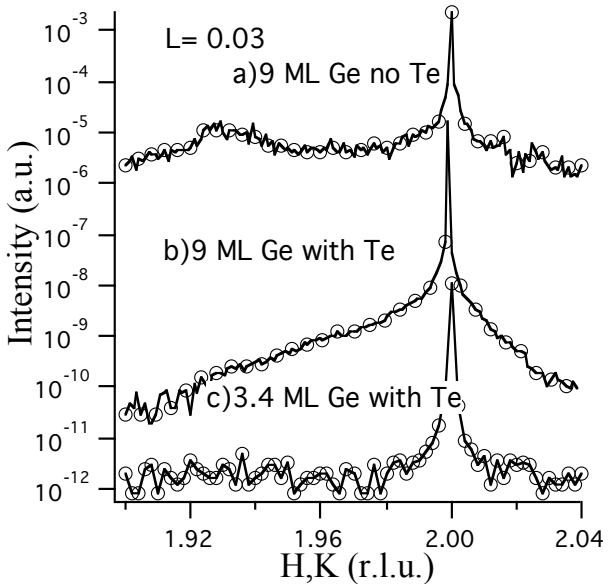

Figure 2. GIXD measurements for 3 different Si/Ge/Si(001) heterolayer structures around the Si (2 2 L = 0.03) Bragg peak. (a) 9 ML Ge with no surfactant (b) 9 ML Ge with Te as a surfactant, and (c) 3.4 ML Ge with Te as a surfactant.

DISCUSSION

Previous grazing incidence diffraction has been performed on Si/Ge/Si(001) samples[9]. Williams *et al* [10] verified that that the critical thickness for strain relaxation is between 3 and 4 ML for Ge growth on Si at 500°C. For 10 ML thick films they found that the strain in the Ge epilayer consisted of both a fully relaxed component as well as a Si-Ge alloy component. Thornton *et al* [11] performed a similar study using Sb as a surfactant and measured the critical thickness for the onset of Ge relaxation to be ~11ML and claim that even up to 55ML the films grown with Sb are at least partially strained. It is apparent from our data that the growth mode for the 9 ML sample grown with Te is pseudomorphic.. This is in contrast to the sample grown without surfactant, which is almost fully relaxed.

It is interesting to compare our results for coherent fraction and coherent position to values as predicated by various growth models. The lattice mismatch between Si and Ge is 4.2%, therefore, if the film is lattice matched in-plane, the film with be tetragonally distorted out-of-plane by an amount as predicted by linear elasticity theory. The strain in the [001] direction is given by:

$$\varepsilon_{\perp} = -2\frac{c_{12}}{c_{11}}\varepsilon_{\parallel} \quad (1)$$

where $c_{11}=12.4\times10^{10}$ Nm^{-2} and $c_{12}= 4.13\times10^{10}$ Nm^{-2} for Ge [12]. Therefore, for a 4.2% contraction in the [010] and [100] direction one calculates a 3% expansion of the film in the [001] direction. This results in a lattice spacing that is 7.2% larger for the Ge layer than for the Si(001) substrate. The atomic distribution function introduced earlier can be written:

$$F_H = \frac{1}{N}\sum_{n=0}^{N-1}\exp(2\pi i(nd+\delta_0)) \quad (2)$$

Where N= the total number of Ge layers, d is the difference in lattice spacing in the [001] direction and δ_o is the offset at the Ge/Si(001) interface. From this equation we can solve for theoretical values for f_H and P_H:

$$f_H=|F_H|D^T_H = \frac{[\sin(\pi Nd)]}{[N\sin(\pi d)]}D^T_H \quad (3)$$

$$P_H=\frac{1}{2\pi}\arg(F_H) = \frac{(N-1)}{2}d+\delta_0 \quad (4)$$

In equation (3), D^T_H is the Dynamical Debye Waller factor. In this study we have used D^T_{004} = 0.94 and D^T_{022} = 0.97 based on values for bulk Ge. Figure 3 and Figure 4 are plots of our 022 and 004 XSW data for samples grown with Te. Notice that up to 9ML our values for coherent fraction and coherent position agree well with values predicted from linear elasticity theory for pseudomorphic growth. As the coverage surpasses 9ML the values from the linear elastic model for coherent fraction drop below 0.4. This is due to an increasingly large geometrical factor as more and more Ge layers are deposited. The geometrical factor takes into account the fact that atoms each successive Ge layer occupy slightly different positions with respect to the Silicon

substrate and thus the coherent fraction becomes lower, even in an ideal defect free film. Therefore, it is more difficult draw conclusions from the XSW data at these higher coverages. A similar XSW study that used Bi as a surfactant reported improved values for f_H than for films grown without Bi. However, the data didn't agree as well with linear elasticity as the present study and other structural models were presented in order to interpret the results[13].

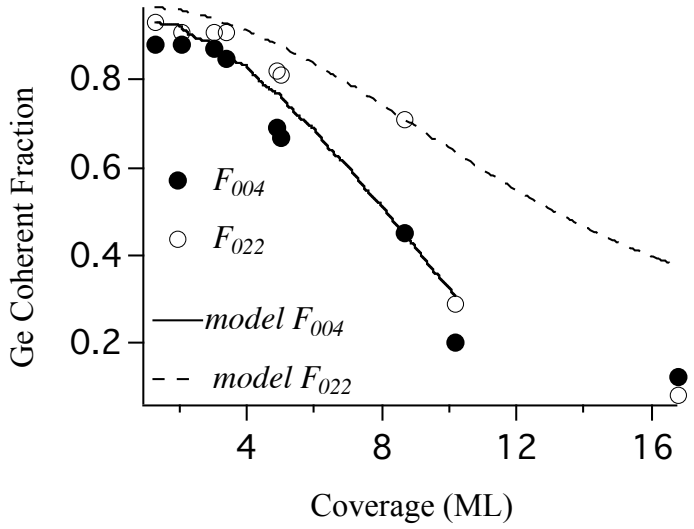

Figure 3. Measured and calculated values for coherent fraction vs. Ge coverage for samples with Te.

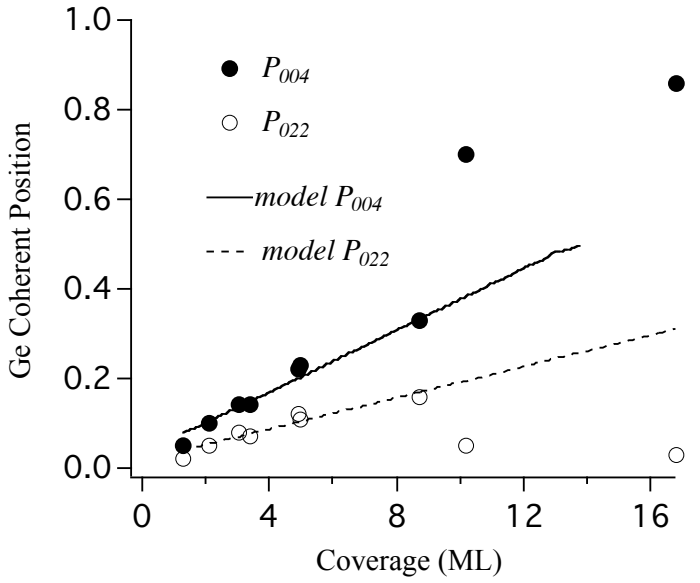

Figure 4. Measured and calculated values for coherent position vs. Ge coverage for samples with Te.

CONCLUSIONS

The efficacy of Te as a surfactant in Si/Ge/Si(001) heterostructures has been verified using both XSW and grazing incidence x-ray diffraction. For samples that were made with Te, the 2-D growth regime was extended to at least 9ML and the data agrees with a linear elastic model for heteroepitaxy. Samples of similar thickness grown without surfactant have a significantly lower coherent fraction implying that either defects are present in these samples or that some degree of intermixing with the silicon capping layer has occurred. Thicker Ge films will eventually be studied to determine the extent to which Te can be effective as a surfactant.

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