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THE EPITAXIAL GROWTH OF Ge ON Si(100) USING Te AS A SURFACTANT

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ABSTRACT

The epitaxial growth of Ge on Si using Te as a surfactant has been studied with high resolution photoemission, low energy electron diffraction and cross-sectional transmission electron microscopy. The growth mode of Ge on Si changed from Stranski-Krastanov to layer-by-layer mode when 1/4 ML Te atoms were on the surface. During the growth, Te atoms segregated to the top of the surface. If the growth temperature is too high (above ~450°C), the Te coverage was less than the necessary coverage to keep the layer by layer growth , and the growth mode of Ge on Si is still S-K.

I. INTRODUCTION

The growth of high quality epitaxial Si-Ge films has recently attracted much attention. The driving force mainly comes from the potential application of Si-Ge alloy and Si-Ge strain layer structures in new generation semiconductor devices, such as high speed electronic and optoelectronic devices [1,2]. It is also of fundamental importance to understand the epitaxial growth process in general; including the interplay among the surface, interface free energy and lattice strain relief. It is well known that the growth mode of Ge on the Si(100) surface is of the Stranski-Krastanov type (i.e. a few uniform layers followed by island formation). Recently, it has been demonstrated that when the growth front is terminated by a specific third species, the surfactant, the Si and Ge growth mode can be dramatically changed. Three dimensional (island) growth can be converted into two-dimentional (layer) growth with the use of surfactant atoms. A number of atoms, such as As, Sb, and Te, have been used as surfactants. [3-9]

Although the surfactant-assistanted Si and Ge epitaxial growth process is under active investigation, the growth mechanism is not well understood. We have studied the growth mechanism at atomic scale for Ge on Si growth with Sb as a surfactant. We found that the Sb atoms saturate the dangling bonds on the Si surfaces and move to the growth front during the Ge growth.[7,8] However, Te is a Group VI element with six valence electrons, while Sb is a group V element with five valence electrons. The surface reconstruction and electronic structure of the Te/Si surface is different from that of Sb/Si. In this work, we investigated the heteroepitaxial growth of Ge on Si(100) using Te as a surfactant under different growth conditions. High resolution core level photoemission, angle resolved photoemission, low energy electron diffraction (LEED) and transmission electron microscopy (TEM) were utilized to characterize the growth process and the grown epitaxial structures. This goal of this work was to understand the effect of the surface on the growth process and the growth mechanism at an atomic scale for surfactant-assisted epi-growth.

II. EXPERIMENT

The photoemission experiments were performed in an ultra-high vacuum chamber (UHV) with a Vacuum Generators (VG) ADES-400 angle-resolved spectrometer at the Stanford Synchrotron Radiation Laboratory. The growth of Ge and Si was conducted in the same

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chamber. The overall instrumental resolution (monochromator plus spectrometer) for the photoemission studies was between 0.2 to 0.25 eV. The chamber had a base pressure less than 2×10^{-10} Torr.

Clean Si(100) surfaces were achieved by the following method. N type Si wafers were chemically precleaned and etched with HF prior to introduction into the UHV chamber. The samples were pre-baked at 600°C for an hour before being heated to 950°C. After cleaning, the Si(100) had a sharp two-domain (2x1) LEED pattern and strong emission from surface states in the valence band spectra. No contamination was observed in the core level spectra. The Te and Ge were thermally evaporated onto the substrate. The thicknesses of the the deposited films were measured by an in situ quartz-crystal thickness monitor. High resolution cross sectional TEM was performed with a Philips 430ST microscope operated at 300kV which had resolution of better than 2Å.

The Ge growth on Si proceeded as follows. A layer of Te was first deposited on the Si surface. The Te/Si(100) 1x1 surface was achieved by either depositing one monolayer of Te atoms on the Si(100) surface at room temperature and then annealing to about 250°C to 300°C or depositing one monolayer of Te atoms at a substrate temperature of about 250°C to 300°C. The Te/Si(100) 2x1 surface was achieved by depositing one monolayer of Te at room temperature and then annealing to the temperature above 450°C. Ge atoms were then deposited on both Te/Si(100) 2x1 surface and Te(100) 1x1 surface at 300°C as well as on Te/Si(100) 2x1 surface at 450°C. Photoemission and LEED measurements were performed at each step of the growth process.

III. RESULTS AND DISCUSSION

In order to understand the Te/Si(100) surface, the adsorption of Te on Si has been investigated. Figure 1 shows the relative photoemission intensity of the Te 4d peak which were taken at the 80 eV photon energy. It can be seen that after a certain time, the Te 4d intensity was saturated. The saturation of the measured Te 4d signal may result from that the sticking coefficient of Te on the Si surface above certain Te coverage approaches zero or simply start island. The saturation coverage of the Te is about 0.6ML which is calculated from the core level peak intensities. In all of our experiments, the Te atoms were deposited on the Si(100) substrate until saturation occurs.

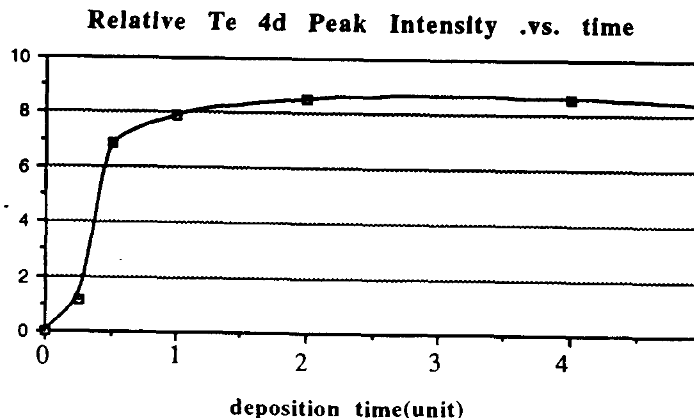
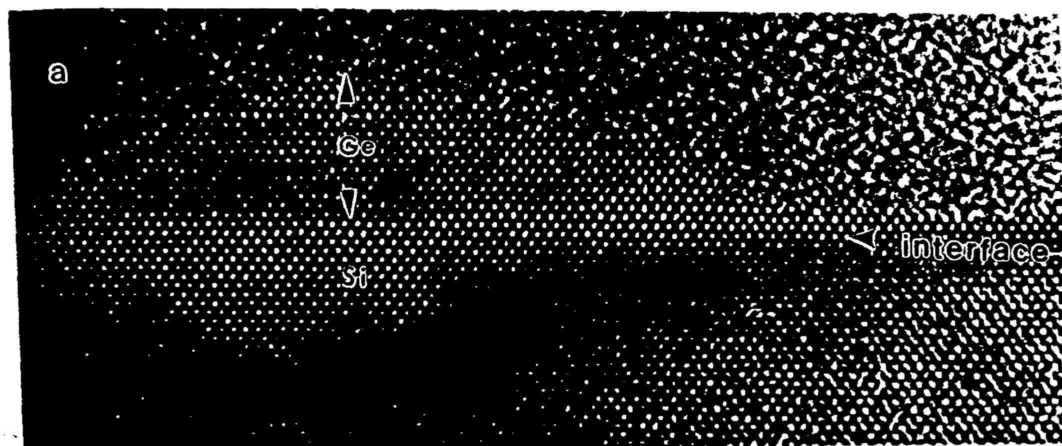


Fig 1: The relative Te 4d peak intensity vs. the Te deposition time. After a certain time, the intensity of Te 4d peak went to the saturation.

Figure 2 shows the high resolution cross sectional TEM micrographs for the structure of Ge on the Te/Si(100) surface. Fig. 2a shows the structure which the Ge was grown on the Te/Si(100) 2x1 surface at 450°C. It is clear from Fig. 2a that the growth mode is S-K under this condition. The islands are epitaxial on the substrate and their sizes are typically larger than several hundred angstroms. Fig. 2b shows the structure which the Ge was grown on the Te/Si(100) 1x1 at 300°C. More than 15 ML of Ge layers is epitaxial on the Si(100) substrate and the growth mode is layer-by-layer. No large islands are observed on the surface. Some defects are observed in the Ge layer which release the strain during the layer-by-layer growth. The defect size is usually only several monolayers.



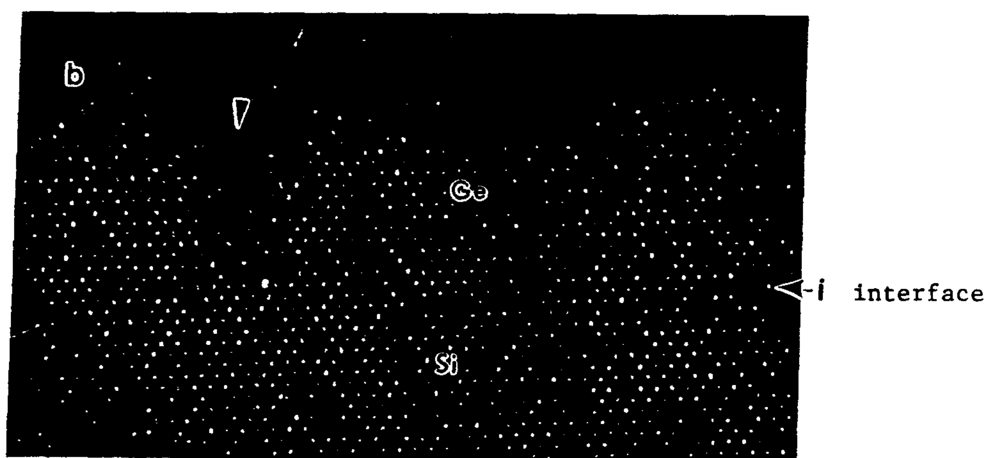
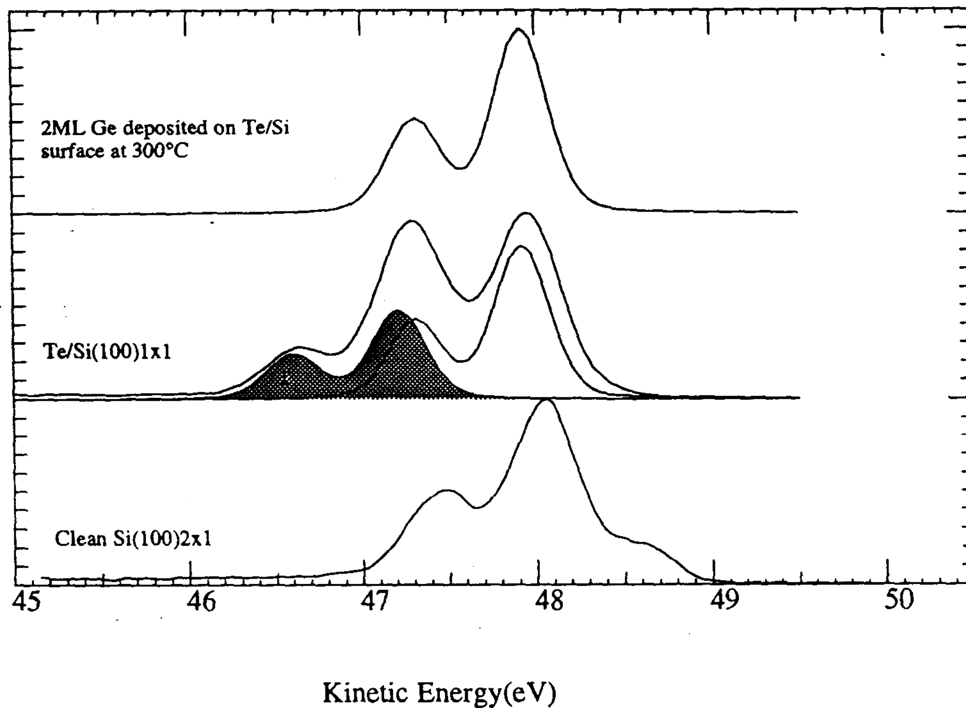


Figure 2: The high resolution cross-sectional TEM micrographs for the grown structures. 2a. Ge was grown on the Te/Si surface at 450°C. 2b. Ge was grown on the Te/Si(100) 1x1 surface at 300°C

During the growth, the Te atoms completely segregate out and leave Si interface. This is proven by the Si 2p core level spectra shown in Figure 3. Figure 3 shows the Si 2p core level spectra for the clean Si(100)2x1, Te/Si(100)1x1 and the surface after 2ML Ge was deposited at Te/Si(100)1x1 at 300°C. The spectra were taken at 150eV photon energy. For the Te/Si(100)1x1 surfaces, Si 2p core level was decomposed to two component , a bulk component (b) and a charge transfer component (r). The component r, which is not observed in the clean Si(100) surface, is the result of charge transfer between the Si and the Te atoms. The shift of r component relative to the bulk component is about 0.73eV to the lower kinetic energy. After 2ML Ge was grown on the surface at 300°C, only the bulk component was observed and the r component was eliminated. This indicated that there is no charge transfer between the Te and Si atoms after the 2ML Ge growth. This means that the Te atoms have segregated out and left the Si interface.

Si 2p Core Level Spectra



Kinetic Energy(eV)

Fig 3: The Si 2p core level spectra for the clean Si(100)2x1, Te/Si(100)1x1 and the surface after 2ML Ge deposited on Te/Si at 300°C. After Ge deposition only the bulk component exists. This indicated that Te atoms had migrated from the Si interface.

Ge can also be epitaxially grown in the layer-by-layer mode on the Te/Si(100) 2x1 surface at 300°C. After 2ML Ge deposition on the Te/Si(100) 2x1 surface at 300°C, the LEED pattern already changed from 2x1 to 1x1 or 1x1 with weak and diffused C(2x2) spots. Figure 4 shows the Te 4d, Ge 3d and Si 2p core level spectra for the growth of 14Å Ge on Te/Si(100) 2x1 surface at 300°C and 450°C. The Te 4d and Ge 3d were taken at the photon energy of 62.5eV and the Si 2p was taken by using the second order light (125eV). After the 14Å Ge was grown at 450°C, the Si 2p core level is still observed. This means that the Si is still present near the surface after 14Å Ge growth and the growth mode must be S-K or islanding. After the 14Å Ge was grown at 300°C, the Si 2p peak was not observed and the Ge 3d orbit splitting was nicely observed. This indicates that the Ge layer is very uniform and there is no Si near the surface. The Ge growth mode must be layer-by-layer growth.

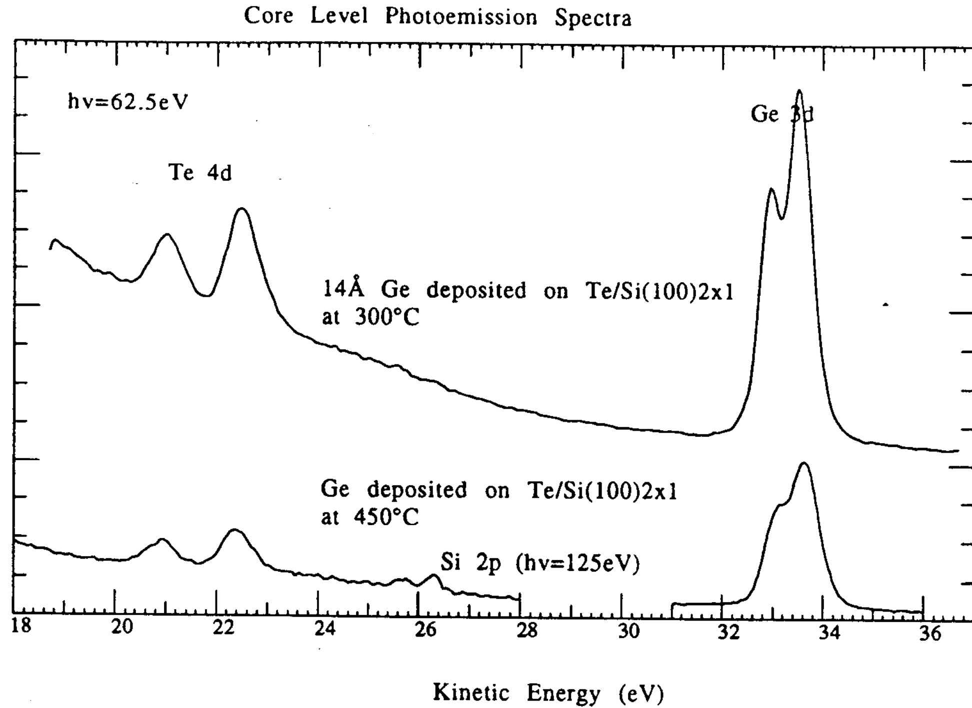


Fig 4: Photoemission core level spectra of Te 4d, Ge 3d and Si 2p for the Te/Ge/Si surfaces. For the growth at 450°C, the Si 2p core level was always observed, it indicated island growth. For the growth at 300°C, the Ge 3d spin orbit split is more clear and the Si 2p core level is eliminated, it indicates that the growth is more uniform.

Table 1. Te 4d relative intensities on different surfaces.

Surface Conditions	Relative Intensities	coverage
Te/Si(100) after 450°C anneal, 2x1 LEED	1	~0.5ML
14Å Ge deposited on the Te/Si(100) 2x1 at 300°C	0.44	~0.25ML
14Å Ge deposited on the Te/Si(100) 2x1 at 450°C	0.14	~0.08ML
Te deposited on the Ge(100) surface at 450°C	0.15	~0.08ML

Table 1 shows the Te 4d intensities for different Te/Si(100) surfaces before and after Ge growth and Te/Ge(100) surface. The amount of Te on the different surfaces is determined from the Te 4d relative intensities. The Te/Si(100) 2x1 surface was covered by about 0.5ML Te atoms. After 14Å Ge was deposited onto the Te/Si(100) 2x1 surface at 300°C, the Te 4d intensity decreased to about 44% of that on the original Te/Si(100) 2x1 surface. This indicated that the Ge/Si(100) surface was covered by about 1/4 ML Te atoms. After 14Å Ge was deposited onto the Te/Si(100) 2x1 surface at 450°C, the Te 4d intensity decreased to about 14% of that on the original Te/Si(100) 2x1 surface. This indicated that the Ge/Si(100) surface was covered by less than 1/12 ML Te atoms. The Te coverage was also measured for the Te/Ge(100) surface for comparison after the Te atoms were deposited onto Ge(100) surface at 450°C. The Te coverage under this condition was determined to be around 0.08 ML.

Both PES and TEM confirm that Ge can grown uniformly at low temperature, while at high temperature, the growth turns to S-K mode. It has been clearly shown from above that the Te can be used as a surfactant even with only 1/4 ML surface coverage. This is quite different from the surfactant growth of Ge on Si using Sb (or other Group V elements) as surfactants.[7] The Sb atoms formed an order layer with one monolayer coverage on the Si(100) surface. During the Ge growth on Sb/Si(100) substrate, Sb segregated out and Ge occupied the epitaxial sites left by the Sb atoms. Most of the Sb atoms still occupied the epitaxial sites on the growth front. In the case of Te as a surfactant, the Te coverage on the surface decreases from the initial about 0.5ML coverage to 1/4ML coverage as the Ge growth proceeds. This shows that the surfactant atoms do not have to occupy all the surface epitaxial sites for the surfactant assisted layer-by-layer growth to happen. However, certain amount of surfactant atoms must remain on the surface to saturate the surface bonds in order to maintain the layer-by-layer growth. In the case of Te, 1/12ML of Te coverage is not enough to maintain the layer-by-layer growth.

IV. CONCLUSION:

The epitaxial growth of Ge on Si using Te as a surfactant has been successfully demonstrated. The Ge can be grown in the layer-by-layer growth mode on both the Te/Si(100) 2x1 and 1x1 surfaces. It has been found that the growth mode of Ge on Si can be changed from Stranski-Krastanov to layer-by-layer mode by only 1/4 ML Te atoms on the surface. During the growth, Te atoms segregated to the top of the surface. If the growth temperature is too high (above ~450°C), the amount of Te coverage will be less than 1/8 ML, and the growth mode of Ge on Si will remain S-K mode. By comparing the Te and Sb as surfactants for Ge on Si growth, it is concluded that the monolayer surfactant coverage on the growth front is not a necessary condition for the surfactant assistant growth.

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