Study of the growth of Au films on Si(100) and Si films on Ge(100) surface

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Abstract

The growth of Au films grown on a Si(100)-2x1 surface and Si films on a Ge(100)-2x1 substrate is studied using Positron-annihilation induced Auger Electron Spectroscopy(PAES), Electron induced Auger Electron Spectroscopy(EAES), and Low Energy Electron Diffraction(LEED). Previous work has shown that PAES is almost exclusively sensitive to the top-most atomic layer due to the trapping of positrons in an image potential well just outside the surface before annihilation. This surface specificity is exploited to profile the surface atomic concentrations during the growth of Au on Si(100) and Si on Ge(100) and EAES provides concentrations averaged over the top 3-10 atomic layers simultaneously. The difference in the probe-depth makes us possible to use PAES and EAES in a complementary fashion to estimate the surface and near surface concentration profiles. The results show that (i) the intermixing of Au and Si atoms occurs during the room temperature deposition, (ii) the segregated Ge layer is observed onto the Si layers deposited at 300K. In addition, the prior adsorption of hydrogen prevents the segregation of Ge on top of the deposited Si and that the hydrogen adsorption is useful in growing a thermally stable structure.

1. Introduction

The ability to characterize the chemical composition of the outer most atomic layer is important to the application of surface analytical techniques and material technology, including the development of growth techniques for high quality films and the development of semiconductor processes involving ultra-thin doping layers. While many techniques are available for the chemical analysis of surfaces, each has its own peculiar combination of sensitivities and limits [1]. The factors determining the surface sensitivity is the probe depth of either the in-coming or out-going beam(or both). Surface spectro-scopic techniques use either electrons or ions of approxi-mately a few keV energies will be intrinsically less surface sensitive by the deep penetration depth due to classical scattering phenomena. Even though the electrons having keV energies penetrate a depth of an order of 1000 Å, the sampling depth of the electron spectro-scopes is limiting by the 5 Å - 20 Å escape depth of the Auger electrons. Further the energetic incident particles create a large secondary background, which makes it difficult to obtain an accurate lineshape, particularly the low energy Auger lines.

Recently, Positron-annihilation induced Auger spectro-scopy(PAES) [2] has been demonstrated that a unique capability to determine unambiguously the elemental composition of the topmost atomic layer without the

problem associated with ion mixing. The enhanced surface selectivity of PAES stems from the fact that positrons implanted into a metal or semiconductor at low energies have a high probability of diffusing back to the surface and becoming trapped in an "image-correlation-well" before they annihilate. The positrons localized at the surface well annihilate almost exclusively with the atoms in the topmost layer and almost all of the annihilation induced Auger electrons originate from the top-most atomic layer [3,4].

In this paper, PAES is used in combination with Electron-induced Auger Electron spectroscopy(EAES) [5] to study the growth of the initial stages of Au thin films on a Si substrate and Si thin films on a Ge substrate. The results of the measurements indicate that the intermixing of Au and Si atoms occurs even during room temperature deposition. The prior adsorption of hydrogen prevented Ge segregation over the deposited Si layers, which were stable over an extended temperature range. Although many surface analysis techniques have been applied to analysis on the topmost surface compositions of Au-Si and Si-Ge systems, the con- centration profile of the surface and near surface com- position is not determined due to the lack of surface sensitivity. Fortunately, using the combination of PAES and EAES in a complementary fashion the surface and near surface concentration profiles can be estimated.

2. Experimental method

The measurements are performed using The University of Texas at Arlington PAES system, which has been described previously [2-4]. The system consists of a magnetically guided positron beam, a trochoidal energy analyzer and a UHV sample preparation and charac-terization chamber, which is also equipped with an EAES and Low Energy Electron Diffraction(LEED) systems. The Si(100) and Ge(100) single crystal wafers are cleaned by multiple Ne$^+$ sputtering(0.5 keV) and annealing (1200 K and 900 K, respectively) cycles, resulting in

a clear (2x1) LEED pattern and no detectable surface contamination as determined by EAES. After cleaning and annealing of the substrate, Si films(Au films) are deposited by evaporating silicon(or gold from a Au evaporator) from a thin silicon rod mounted on molybdenum leads. The rectangular rod(0.2 cm × 0.2 cm × 2 cm) is cut from a Si(100) wafer and connects at each ends to a 0.1 cm-diam Mo-wire. After outgassing, the chamber pressure remained at ~5 × 10^{-10} Torr during evaporation and at ~2 × 10^{-10} Torr during the PAES measurements. The amount of Au or Si coverages, measured in equivalent monolayers(eq. ML) is determined from the deposition time at a fixed deposition rate established using a quartz crystal thickness monitor. One eq. ML is defined as a deposition of the number of atoms per unit area in a bulk (100) atomic layer. EAES spectra are also taken to check the calibration used in depositing the Au(or Si) and to periodically monitor surface contami-nation.

Molecular hydrogen(purity 99.999%) is admitted into the chamber through a Granville-Phillips leak valve by which means the hydrogen pressure in the chamber is maintained at ~10^{-5} Torr during hydrogen exposure of the sample. Dissociating molecular hydrogen at the ion-gauge can form atomic hydrogen as indicated in the ref. [6]. The exposure in Langmuirs(L) is determined by taking the ion gauge reading in Torr after back-filling and multiplying by the time in seconds and 10^6/R$_g$, where R$_g$ is the relative efficiency of the ion gauge for the appropriate gas taken from ref. [7] (R$_{H2}$ =2.2). The concentrations of Si and Ge in the top most layer are determined by comparing PAES spectra obtained from the overlayer system with reference spectra for Si and Ge. Details of the methods for the determination of surface concentrations are given in ref. [8], in the case of the PAES data, and in ref. [9], in the case of the EAES data. Both the PAES and EAES calculations assume the concentrations to be a function of the ratio of the Si and Ge Auger inten-sities and that the Si and Ge concentrations add to 100%.

3. Result and discussion

3.1 Estimation of the concentration profile of the Au/Si interface

In an effort to extract atomic concentration profile from the complementary PAES and EAES data, model structures of the Au/Si interface as shown in Fig. 1 are constructed schematically such that the PAES and EAES intensities calculated from these structures would match the measured values. The EAES intensities are assumed to reflect a weighted average of the atomic concentrations of many atomic layers calculated from model structures using Eq. (1):

$$I_i = I_i^0 \left(1 - \exp\left(\frac{-d}{\lambda \cos\phi}\right)\right) \times \sum_{n=0}^{20} C_{n,i} \exp\left(\frac{-nd}{\lambda \cos\phi}\right) \tag{1}$$

where I_i is the intensity of the Auger signal from the ith element(in this case Au or Si) for the composite system, I_i^0 is the Auger intensity for the pure element "i" (Au), n is the layer number, d is the thickness of an atomic layer, $C_{n,i}$ is the atomic concentration of the ith element in the nth layer, λ is the electron inelastic mean free depth(assumed to be composition independent), ϕ is the angle of the outgoing electron with respect to the sample normal and z is the depth into the material. The choice of the top layer concentrations in the model structures is guided by the PAES results. The sum is truncated at 20 atomic layers to simplify calcu-
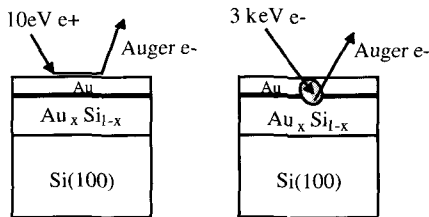

Fig. 1 Schematic illustrating the difference in the probe-depth of the PAES and EAES techniques from the Au-Si system. The chemical structure can be explained by both PAES and EAES spectra taken from the surface where 8 ML Au deposited on Si(100) surface shown in fig. 2.

lation. The calculated values of I_i for Au and Si are then inserted into Eq. (2) to obtain averaged concentrations from modeled EAES intensities(a more complete discussions of the approximations used in Eq. (1) may be found in reference [3]).

$$C_x = \frac{(I_x/I_x^0)}{[(I_{Si}/I_{si}^0) + (I_{aAu}/I_{Au}^0)]} \tag{2}$$

where C_x is the averaged surface concentration where x=Au or Si, and I_{Au} and I_{Si} are the measured Auger peak-to-peak heights for Au and Si, respectively. The EAES data do not provide enough information to infer a unique concentration profile. Simple profiles are chosen for lack of information to the contrary. It is reasonable to believe that the true structures share some of the basic features of these simple models.

Figure 2 shows the PAES and EAES spectra at four different coverages of Au deposited onto the clean,
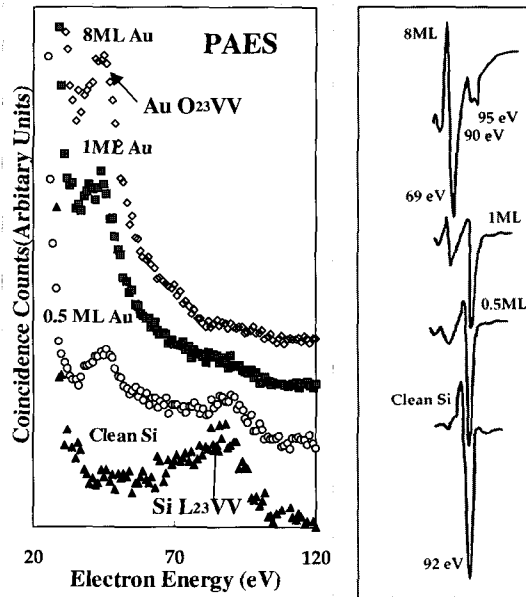

Fig. 2. PAES spectra obtained from a clean Si, 0.5 ML Au/Si, 1 ML Au/Si, and 8 ML Au/Si surfaces at 303 K. As high coverages of Au, the Au Auger peak grows while the Si peak decreases. This trend is found in both PAES and EAES.

reconstructed Si(100) surface at room temperature, namely: 0 ML [clean Si(100)], 0.5 ML, 1 ML, and 8 ML. As the Au coverage increases the PAES Au $O_{2,3}$ VV transition (~43 eV) increases and the PAES intensity due to the Si $L_{2,3}$VV (~88 eV) transition decreases. The electron-induced Au (69 eV) and Si $L_{2,3}$VV Auger peaks (92 eV) in EAES show the same trend as in PAES. However, the decreases in the peak intensities are less pronounced due to the deeper probe depth of EAES. In the EAES spectrum, a splitting of the 92 eV peak is still observed after 8 ML of Au deposited on Si(100) surface while no Si peak is apparent in the PAES spectrum. Taken together, the surface is completely covered by Au layers with several Au-Si intermixing layers underneath as shown in Fig. 1.

3.2 The effect of adsorbed atomic hydrogen on the growth of ultra-thin Si films on Ge(100) substrate

The atomic profile of segregated Ge is modeled in an attempt to account for both PAES and EAES data in Fig. 3. Since PAES provides concentration information almost exclusively from the top layer and EAES measurements provide information regarding an averaged concentration summed over 3-8 layers and weighted by the electron escape probability from each layer. It is possible to draw conclusions concerning the concentration profiles for the thin film structure by requiring that modeled intensities be consistent with both PAES and EAES data.

The Si/Ge(100) system is modeled as a successive number of atomic layers. The modeled PAES concentration is taken to be the Ge concentration of the

Model A   Model B   Model C
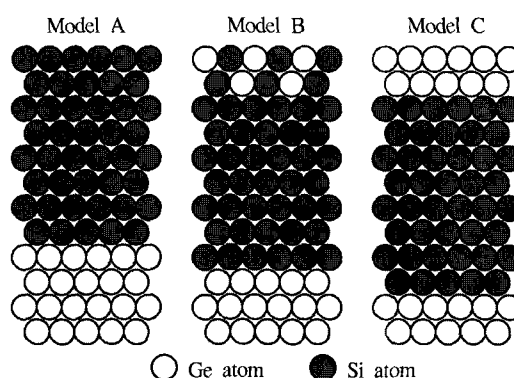
○ Ge atom   ● Si atom

Fig. 3. Models(schematic) of the atomic concentrations at a Ge surface after 8 ML Si deposition.

topmost atomic layer of the model structure. The modeled EAES concentration is determined from EAES intensities calculated using Eqs. (1) and (2). The estimated and calculated atomic concentrations from the model structures are summarized in Table 1. Model A consists of 8 ML of Si placed on top of the Ge substrate. In model B, 50% of Ge and 50% of Si atoms are in the first and second layer, the third through ninth layers are Si and the deeper layers are all taken to be Ge. In model C we assume that 8 ML of Si layer is sandwiched between 2ML of Ge on the surface and the Ge substrate. The modeled concentration from model A is in agreement with the case of 8 ML of Si deposited on Ge(100) substrate at 173 K and H saturated Ge(100) surface. The measurement obtained from 8 ML of Si deposited on Ge at 300 K without H gives estimated concentrations consistent with model B. The measurements obtained from 8 ML Si deposited on Ge at 830 K and annealed at high temperature are consistent with model C.

The effectiveness of atomic hydrogen in preventing Ge segregation to the surface is investigated by comparing

Table 1. Summary of the estimations from Models.

Model	I_{Si}(PAES)	I_{Si}(EAES)	Remark
A	100% Si	66% Si	8ML Si/Ge(100) deposited at 173 K 8ML Si/H/Ge(100) deposited at 300 K
B	50% Si	63% Si	8ML Si/Ge deposited at 300 K
C	0% Si	28% Si	8ML Si/Ge deposited at 830 K annealed 8 ML Si/Ge at 830 K

PAES measurements on surfaces prepared by depositing ultra-thin films of Si on the Ge substrate with and without prior H adsorption. Fig. 4 shows the measured PAES and EAES intensities of the Si LVV and Ge MVV peaks after deposition of 8 ML of Si on Ge (100) with (fig.4(c)) and without(Fig. 4(b)) the prior adsorption of hydrogen on the substrate. In the case of prior exposure to 2500 L of hydrogen, the surface
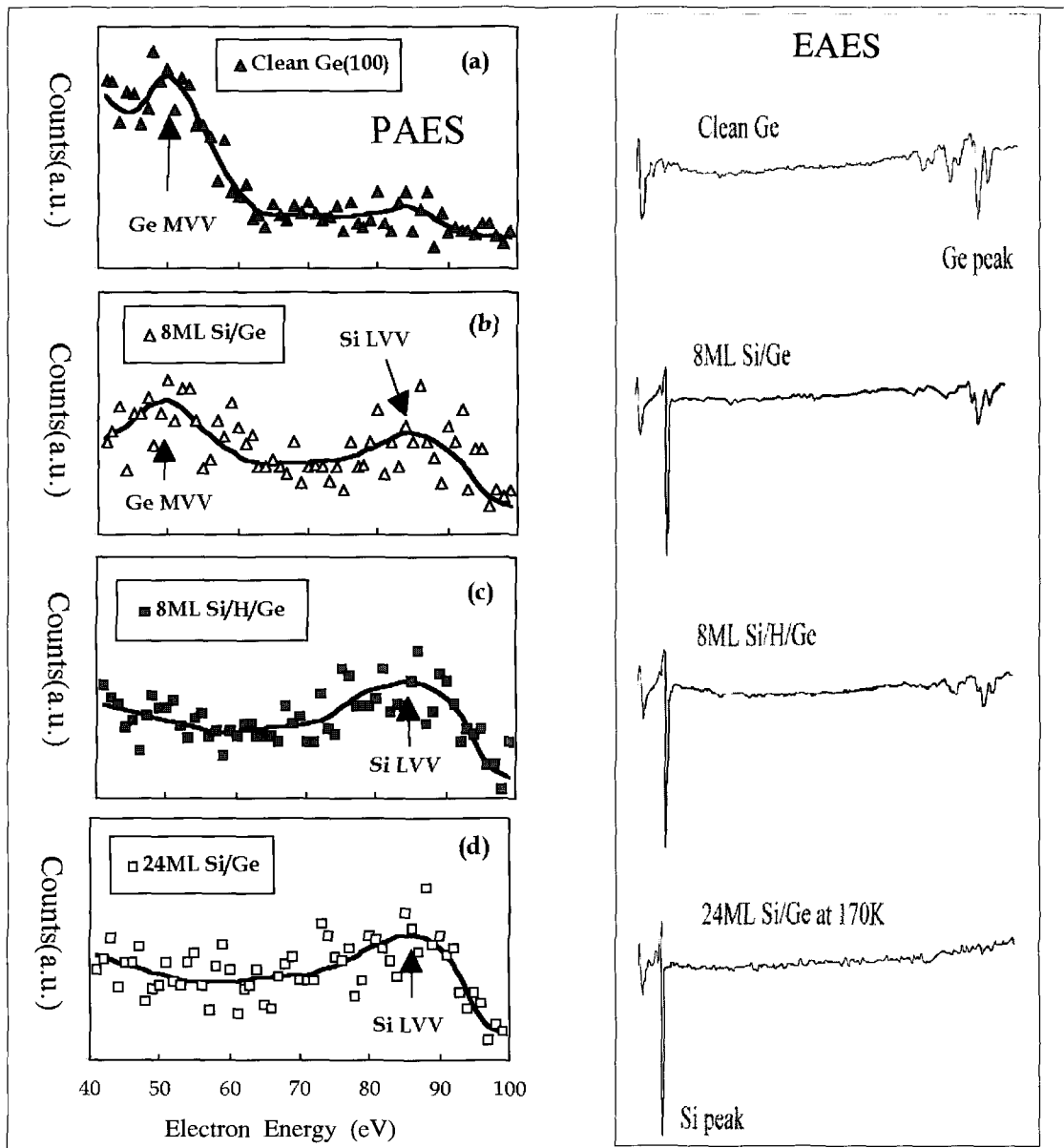

Fig. 4. PAES and EAES spectra measured after deposition of 8ML of Si on Ge(100) without(b) and with(c) the prior adsorption of H on the substrate. Fig 3(a) and (d) are PAES and EAES spectra taken from a clean Ge(100) at 300 K (a) and the Si reference surface at 173 K (d), respectively. The solid line were obtained by fitting the data using two-parameter linear least-square fit, extracting the relative contributions of Si and Ge contributed to the PAES spectra.

concentration of Si was observed to be 98% using PAES(71% Si using EAES).

The reason for the apparent discrepancy between the PAES and EAES results can be understood in terms of the difference in probe depth of the two techniques. PAES information comes almost exclusively from the top-most atomic layer while EAES provides information averaged over the top 3-10 atomic layers. This difference in probe depth of PAES and EAES makes it possible to model the surface and near surface concentration profiles. The PAES and EAES results after prior H adsorption are consistent with intensities calculated using a model in which the topmost layer is almost completely Si. In contrast, the results obtained for room temperature deposition of Si on the clean Ge substrate are consistent with a model in which the top layer concentration of Si is less than 50%. The PAES results provide a clear indication that prior hydrogen exposure can prevent Ge segregation to the surface of 8 ML Si layers on Ge(100).

Summary

By making use of the surface selectivity of PAES, it was possible to directly monitor the compositional changes in the topmost atomic layer as a function of the quantity of Au (or Si) deposited. The results of the PAES measurements indicate that the intermixing of Au and Si atoms occurs even during room temperature deposition. PAES also is applied in the study of the effect of adsorbed atomic hydrogen on the stability of Si films grown on a Ge(100) substrate. The concentration of Si and Ge atoms on the surface layer is monitored by measuring the ratio of the PAES intensities of the Si LVV and Ge MVV peaks after deposition of Si on Ge(100) with and without the prior adsorption of H on the substrate. The PAES results show that the prior adsorption of hydrogen prevented the segregation of Ge on top of the deposited Si and that the hydrogen adsorption was useful in growing a thermally stable structure.

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