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Effect of annealing on a Ge thin film on a Si(111)7×7 surface: A study using ARUPS, XPD, and LEED

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To study the changes in structure and morphology of a Ge thin film as a function of annealing temperature, we implemented complementary surface analysis techniques such as angle-resolved ultraviolet-photoelectron spectroscopy, x-ray-photoelectron diffraction (XPD), and low-energy electron diffraction. The Ge thin film (≈ 15 Å) was obtained by exposing a Si(111)7×7 surface to catalytically decomposed germane at room temperature. The amorphous-crystalline transition temperature was found to be close to 400 °C. A 5×5 reconstruction of the Ge surface occurred for a 500 °C annealing temperature and remained stable to 600 °C. This 5×5 surface reconstruction appeared to have an effect on the XPD curve recorded along the $\bar{\Gamma}$-$\bar{M}$ line in the 1×1 surface Brillouin zone. A 2.5° shift of the peak located near 55° was observed along the $[\bar{1}2\bar{1}]$ azimuthal direction. Annealing at 700 °C led to the indiffusion of Ge into Si or to Ge islanding: the 5×5 surface reconstruction turned into a 7×7 surface reconstruction.

I. INTRODUCTION

A large number of studies have dealt with the Ge/Si heterostructure over the last decade, mainly because of its interesting optical and electrical properties. Nevertheless it must be noted that the greater part of these investigations concerned Ge growth on the Si(111)7×7 substrate by molecular-beam epitaxy (MBE) and solid-phase epitaxy (SPE).[1-5] It is well known that Ge growth on Si(111)7×7 is a Stranski-Krastanov [two dimensional (2D), three dimensional (3D)] growth mode, and the critical thickness of the Ge-deposited film seems to depend closely on the conditions of preparation. Conversely, despite the fact that the low-pressure chemical-vapor-deposition (LPCVD) technique allows a multiple-wafer treatment, and that it can be implemented easily, the growth of Ge on a Si(111)7×7 surface has received little attention.[6] However, the structure and morphology of a deposited film are well known to depend closely on the growth conditions; the initial stages of Ge thin-film formation by LPCVD and MBE techniques are quite different.

Thermal and catalytic decomposition of germane on a Si(111)7×7 surface has been studied in a previous report,[7] and the Ge_xH_y radicals involved in the adsorption mechanisms experimentally identified by photoemission techniques. The present work focuses on a study of the structural and morphological changes in a Ge thin film obtained by LPCVD at room temperature as a function of annealing temperatures. A clean Si(111)7×7 substrate was exposed to catalytically decomposed germane (GeH_4^*) and subjected to annealing at various temperatures. After exposure and after each annealing, the sample was probed with various complementary surface analysis techniques, such as angle-resolved ultraviolet-photoelectron spectroscopy (ARUPS), x-ray-photoelectron diffraction (XPD), and low-energy electron diffraction (LEED).

II. EXPERIMENTAL PROCEDURE

Experiments were performed in an ultrahigh vacuum apparatus consisting of interconnected preparation and analysis chambers kept at a basic pressure in the low 10^{-10}-Torr range. The analysis chamber was equipped with LEED facilities, an LS 10 hemispherical analyzer, and x-ray (Mg $K\alpha$:1253.6 eV and Al $K\alpha$:1486.6 eV) and ultraviolet (He I:21.2 eV) sources for photoemission investigations.

Moreover, it was possible to rotate the sample holder so as to change the Θ polar and Φ azimuthal angles, thus allowing ARUPS and XPD recording. The Θ polar and Φ azimuthal angles were defined as shown in Fig. 1, along with the geometrical configuration of the analyzing system.

Si(111)-*p*-doped substrates ($\rho \approx 10\ \Omega$ cm, 13×17 mm^2) were first and foremost subjected to Ar^+-ion bombardment and annealing (at 850 °C) cycles, in order to obtain a clean surface. The surface cleanliness was controlled by XPS (x-ray-photoelectron spectroscopy) measurements and reconstruction by LEED presenting a sharp 7×7 pattern, as well as by UPS.

The clean Si(111)7×7 surface was then exposed to 10^4-L GeH_4^*(1 L$=10^{-6}$ Torr×1 s) at room temperature. The gas source was germane with a purity of 99.999%. Catalytic decomposition of germane was achieved by a hot tungsten filament heated at 1600 °C. The tungsten filament and the Si(111) wafer were 5 cm apart. It should be noted that in all our experiments, no tungsten contamination of the studied samples was detected by XPS. The thickness of the Ge-deposited film could be estimated by measuring Si(2*p*) and Ge(3*d*) signals. Thereafter, the substrate was subjected to Joule effect annealings (during 2 min) at different temperatures varying from 200 to 700 °C. Substrate temperatures were controlled by a Cr-Al thermocouple fixed at the back of the sample, and by pyrometry, with a ±50 °C accuracy.

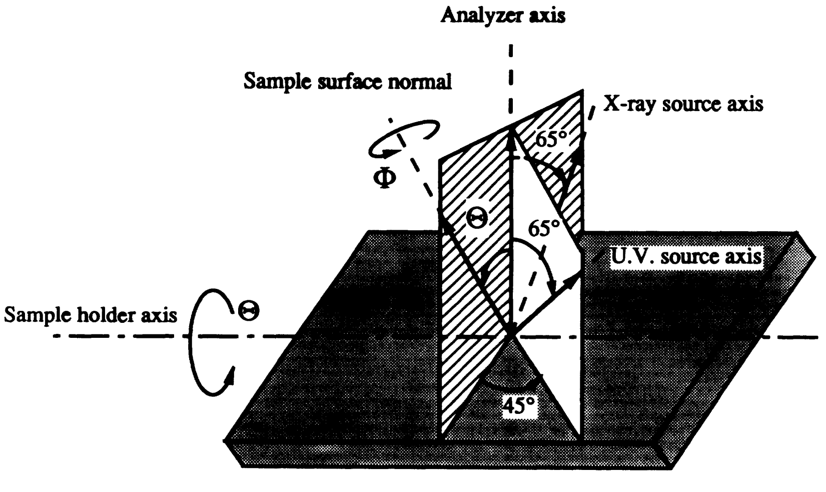

FIG. 1. Schematic representation of the geometry of the analyzing system. The polar angle Θ and azimuthal angle Φ can be varied by rotating the substrate on the holder axis and the surface normal of the sample.

III. RESULTS AND DISCUSSIONS

The ARUPS spectra as well as the XPD spectra presented here were recorded along the [$\bar{1}2\bar{1}$] azimuthal direction corresponding to the $\bar{\Gamma}$-$\bar{M}$ line in the 1×1 surface Brillouin zone (SBZ) of Si(111).

A. Clean Si(111)7×7 surface

In the ARUPS spectra obtained from a clean Si(111)7×7 surface, we mainly observe the three surface states S_1, S_2, and S_3 which are characteristic of the 7×7 reconstruction of the Si(111) surface. It has been established theoretically[8] and experimentally[9] that S_1, located 0.2 eV below the Fermi level E_F, and S_2, located 0.8 eV below the Fermi level E_F, are due, respectively, to the dangling bonds of the adatoms and the restatoms in the unit cell of the Takayanagi dimer-adatom-stacking (DAS) fault model,[10] while S_3, which is located at 1.8 eV below E_F, is attributed to the adatom backbonds.

With our experimental configuration, and within the emission angle range of [0°,20°], S_1 and S_2 surface states are most visible at an emission angle close to 10°, while S_3 can clearly be observed only at $\Theta > 10°$. We could also draw attention to the small energy dispersion of the two surface states toward lower binding energies when the emission angle increases. Indeed, S_1 and S_2 surface states are located at 0.3 and 0.9 eV, respectively, below E_F at normal emission, whereas at an emission angle around 20° their binding energies are 0.2 and 0.8 eV, respectively, below E_F. All these results seem to be consistent with those reported by Märtensson *et al.*,[11] who observed that S_1 and S_2 surface states are at a maximum at $\Theta = 15°$, while S_3 is not visible at $\Theta < 15°$. Such a surface presents an intense (7×7) LEED pattern related to its reconstruction.

As for the XPD curve, the polar angle intensity distribution for Si(2*p*) emission [Fig. 2(a)] particularly exhibits two peaks, at $\Theta = 0°$ and 55°. These features can be very well described by the zeroth-order forward scattering model.[12] Indeed, Fig. 3 shows that in the [$\bar{1}2\bar{1}$] azimuthal direction, there are essentially two internuclear axes (at 0° and 54.7°) along which Si(2*p*) photoelectrons are scattered forward leading to an enhancement of the Si(2*p*) intensity in those directions. It should be noticed that in this forward scattering model, a peak could be expected in the [131] direction, i.e., at an angle of 29.5°, but instead of this maximum we observe a minimum at this energy. This phenomenon has also been reported in the studies of Bischoff *et al.*[13] and Pirri *et al.*[14] This can be explained by destructive interference at high energy, as concluded by Gewinner *et al.*[15] from their single-scattering calculations.

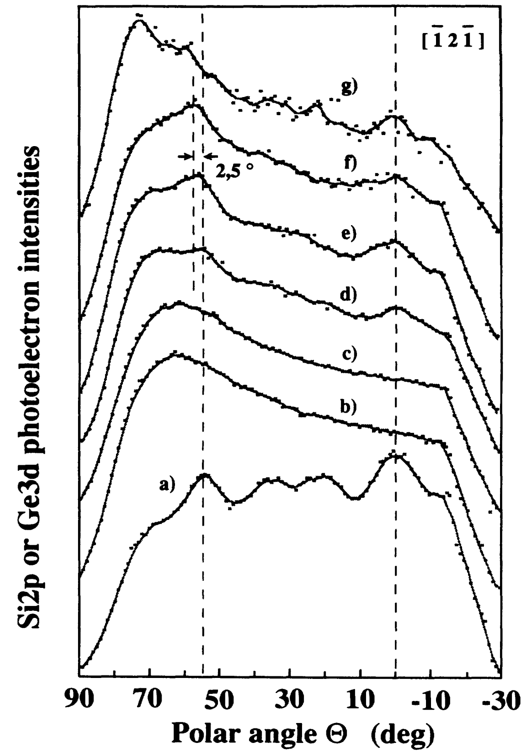

FIG. 2. Polar angle distributions for Si(2*p*) emission intensities obtained from a clean Si(111)7×8 (a), Ge(3*d*) emission intensities obtained after exposure to 10^4 -L GeH_4^* at RT (b), and annealings of the deposited film at 200 °C (c), 400 °C (d), 500 °C (e), 600 °C, (f), and 700 °C (g).

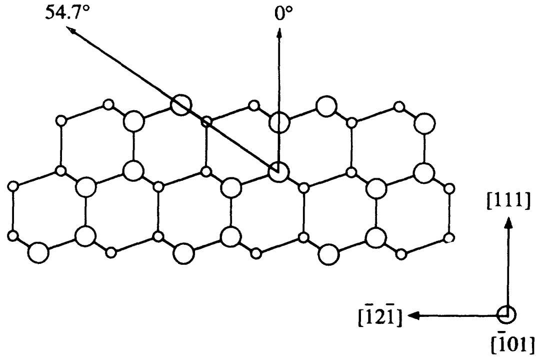

FIG. 3. Representation of the theoretical atomic positions in the [$\bar{1}2\bar{1}$] azimuthal direction. Internuclear axes along which photoelectrons can be scattered forward are represented.

B. Exposure to 10^4-L GeH$_4^*$

After exposure of the clean Si(111)7×7 surface to 10^4-L GeH$_4^*$ at room temperature, the UPS spectrum at $\Theta = 20°$ [Fig. 4(b)] exhibits a large peak located at around 5.5 eV below E_F which supports the presence of GeH, GeH$_2$, and GeH$_3$ species at the surface.[7] It is noteworthy that this large peak is not observed at a normal emission angle. Assuming the exponential decay of the Si($2p$) photo electron intensities, and the hypothesis of a homogeneous thin film, the thickness of the Ge-deposited film is found to be of about 15 Å. The polar-angle intensity distribution for Ge($3d$) photoelectron emission [Fig. 2(b)] reveals no structure in this case. Indeed, the XPD curve from this deposited film simply corresponds to the instrument response function obtained from an amorphous thin film. This result is confirmed by LEED analysis, which shows no electron diffraction but only a high background in the energy range of 20–60 eV. All these observations were to be expected, since it is obvious that the adsorption of GeH$_4^*$ at room temperature on a Si(111)7×7 surface should lead to the formation of a polygermane thin film.

C. Annealing at various temperatures

An annealing at 200 °C of the previously obtained film introduces no significant change in the Ge($3d$) XPD curve, just as there is no significant decrease in the Ge($3d$) intensity. Furthermore, LEED analysis still shows no electron diffraction. Nevertheless, on the UPS spectrum [Fig. 4(c)] recorded at $\Theta = 20°$ we notice the disappearance of the previously observed peak located at 5.5 eV below E_F. This suggests that at this temperature, Ge$_4$H$_y$ radicals are thermally decomposed, leading to the desorption of hydrogen and the formation of an amorphous Ge thin film.[7] The UPS spectrum [Fig. 4(c)] therefore corresponds to the valence-band electronic structure of an amorphous Ge thin film.

The XPD curve and UPS spectrum, as well as the LEED pattern, obtained after annealing at 300 °C, are very similar to those obtained at 200 °C. These observations suggest that, at this 300°C annealing temperature, the Ge-deposited film still remains amorphous.

In contrast, at an annealing temperature of 400 °C, the (1×1) spots are clearly visible on the LEED pattern at an energy of 39 eV. At this temperature, the XPD curve [Fig. 2(d)] presents two peaks at 0° and 55°, as in the case

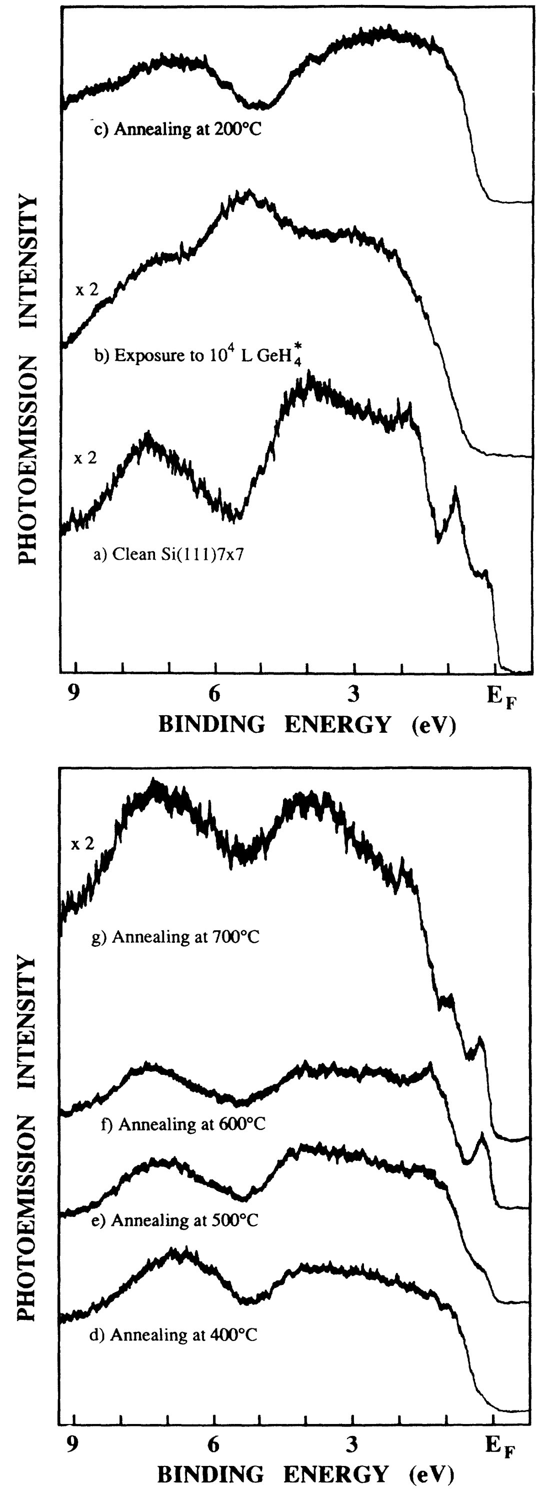

FIG. 4. UPS spectra obtained from a clean Si(111)7×7 (a) ($\Theta = 10°$), after exposure to 10^4-L GeH$_4^*$ at RT (b) ($\Theta = 20°$), after annealings at 200 °C (c) ($\Theta = 20°$), 400 °C (d), 500 °C (e), 600 °C (f), and 700 °C (g) ($\Theta = 10°$).

of the XPD curve obtained from Si(111). These structures can be interpreted as due to Ge($3d$) photoelectrons from inner Ge-layer atoms being scattered forward by top Ge-layer atoms. From these considerations, it seems that we are here in the presence of an epitaxial Ge film. The valence-band electronic structure of such an ordered Ge film is obtained by recording the UPS spectrum [Fig. 4(d)] ($\Theta = 10°$). No surface state is observed in this UPS spectrum, which is to be expected since the Ge surface is not yet reconstructed at this temperature, as shown by LEED analysis.

At an annealing temperature of 500 °C, the previous (1×1) pattern transforms into a (5×5) pattern, suggesting the (5×5) reconstruction of the surface. The UPS spectrum at $\Theta = 10°$ of such a surface is presented in Fig. 4(e). Two surface states S'_1 and S'_2 can be observed, but they are not clearly visible. Moreover, the XPD curve [Fig. 2(e)] obtained from such a film still presents the same two peaks (as in the previous case), but it should be noted that there is a small shift concerning the peak near 55°.

The XPD curve [Fig. 2(f)] related to an annealing at 600 °C is very similar to that obtained at an annealing temperature of 500 °C, except for two aspects. First, the shift of the peak located near 55° becomes more obvious, and is evaluated to be about 2.5°. Second, Ge($3d$) photoelectron intensities significantly decrease for all emission polar angles. At this temperature, LEED analysis shows a sharp and intense (5×5) pattern at an energy of 40 eV. In the same way, the two surface states S'_1 and S'_2 become clearly visible on the UPS spectrum [Fig. 4(f)]. Figure 5 presents the behavior of the two surface-state structures along the $\bar{\Gamma}$-$\bar{M}$ line for emission angles varying from 0° to 20°. We have principally observed two surface-state structures. The first one, located at 0.2 eV below E_F, seems to be nondispersive in the emission range of [0°,20°] and is very intense at $\Theta = 10°$. The second one, located at 1.3 eV below E_F, is not clearly visible at normal emission. It could only be observed at $\Theta > 10°$, and does not seem to present any energy dispersion. These results seem to be in agreement with those of Märtensson *et al.*[11] who also reported ARUPS spectra obtained from the Ge-Si(111)5×5 surface along the $\bar{\Gamma}$-$\bar{M}$ line.

Annealing at a temperature of 700 °C transforms the previous (5×5) LEED diagram into a (7×7) pattern which is not unlike the one obtained from a clean Si(111)7×7 surface. ARUPS spectra recorded along the $\bar{\Gamma}$-$\bar{M}$ line for Θ varying from 0° to 20° are similar to those of the Si(111)7×7 surface. Indeed, as in the case of Si(111)7×7, we can observe three surface states. Nevertheless, we notice some differences between the two cases. First, the S_1 surface state seems to be nondispersive in this emission angle range, and is located at 0.3 eV below E_F. Second, the S_2 surface state also presents energy dispersion, but in this case, the initial energy value is 1.1 eV below E_F [0.9 eV in the case of clean Si(111)7×7] at normal emission, and the final energy value is 0.9 eV below E_F [0.8 eV in the case of clean Si(111)7×7] at $\Theta = 20°$. As for the XPD curve, the two previously existing peaks at 0° and 55° disappear. Furthermore, the general profile of the XPD curve has changed drastically. Indeed, we can observe that the Ge($3d$) photoelectron signal at large emission polar angle ($\Theta = 70°$) is more than twice as high as the Ge($3d$) photoelectron signal obtained at normal emission. This effect did not occur in all the previous cases (annealing at temperatures < 700 °C).

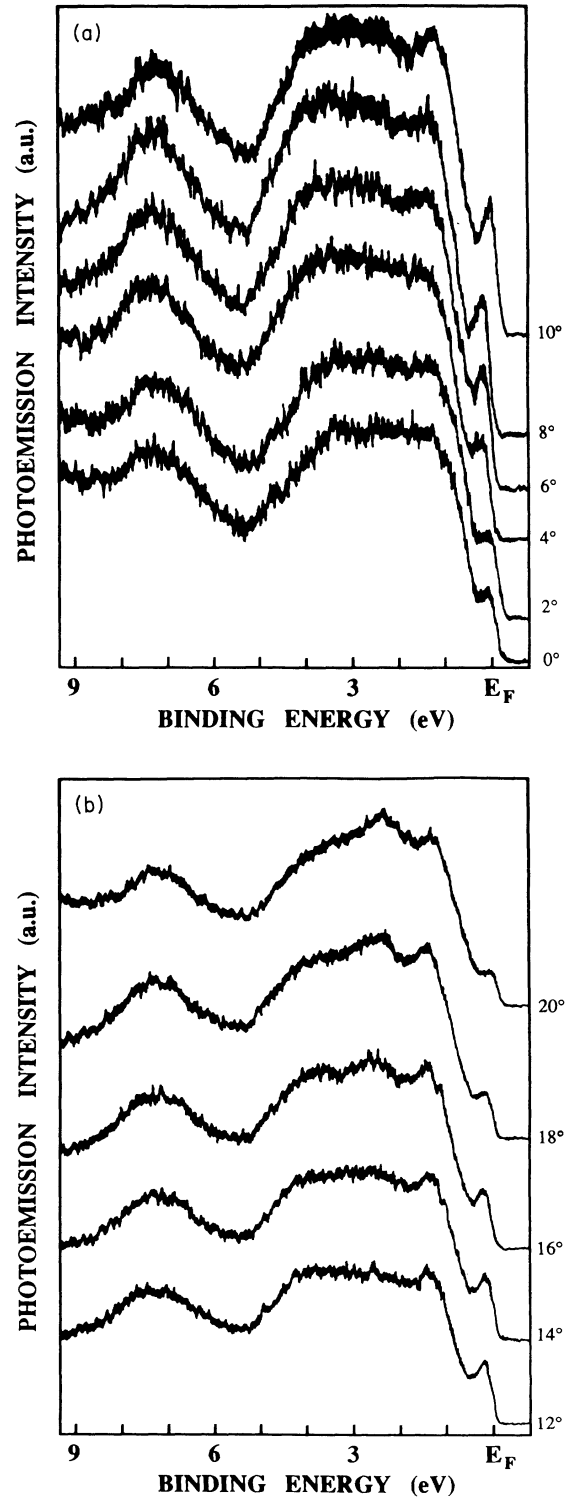

FIG. 5. ARUPS spectra of the Ge-Si(111)5×5 film (obtained after annealing at 600 °C) recorded along the $[\bar{1}2\bar{1}]$ azimuthal direction for (a) $0° < \Theta < 10°$ and (b) $12° < \Theta < 20°$.

D. Discussion

Our results clearly show that exposing a clean Si(111)7×7 surface to 10^4-L GeH_4^* at room temperature (RT) leads to the formation of a polygermane thin film with a thickness of about 15 Å. An annealing at 200 °C desorbs hydrogen, and the polygermane thin film transforms into an amorphous Ge thin film. Moreover, this Ge thin film seems to be stable up to an annealing temperature of about 300 °C. In a recent report, Shinoda *et al.*[16] investigated the surface structural changes during the initial growth of Ge on Si(111)7×7 by solid-phase epitaxy (SPE). From their reflective high-energy-electron diffraction (RHEED) pattern and transmission-electron microscopy (TEM) images, they found that for Ge coverage in the range $\Theta_c - 10$ Å (Θ_c being the critical thickness), and at annealing temperatures above 200 and 450 °C, 3D island formation occurred, and that a δ7×7 pattern could be observed. Nevertheless, our experiments suggest no evidence of island formation for annealing temperatures ranging from 200 to 600 °C, since no change in the general profile of the XPD curves could be detected. Furthermore, the amorphous-epitaxial transition temperature seems to be close to 400 °C. Indeed, at this temperature, the XPD curve presents the same peaks as for crystalline Si(111), suggesting that Ge atoms' local environment is the same as that for Si atoms. In addition, LEED analysis of such a Ge film exhibits an intense and sharp (1×1) pattern.

Two reasons can be given for these differences. On the one hand, there is the fact that our growth technique basically differs from that used by the authors of Ref. 16. Indeed, the first stages of growth are not quite the same, and we particularly believe that in our case hydrogen plays an important part not only in Ge adsorption mechanisms, but also in the structural changes of Ge film deposited by LPCVD. On the other hand, the annealing time in our experiments is about 2 min, while it varied from 1 to 60 min in the work of Ref. 16. Thus it is not surprising that different results are obtained, since it is obvious that both kinetics and thermodynamics are involved in phase-transition phenomena.

The (1×1)–(5×5) surface reconstruction transition is found to occur at an annealing temperature close to 500 °C. The (5×5) Ge-Si(111) has also been observed by many authors.[1,4,11,16] In our experiments, the (5×5) pattern remains stable up to an annealing temperature of 600 °C, at which it becomes intense and sharp, assuming an improvement of the crystallinity of the surface. In the same way, Ge(3*d*) photoelectron intensities significantly decrease at all emission polar angles, but no evidence of island formation has been observed. Consequently, this decrease is probably due to the diffusion of Ge into Si at the interface, and the higher the annealing temperature the more diffuse the Ge-Si interface will become.

Nevertheless, from the attenuation of Ge(3*d*) signals and the increasing of Si(2*p*) signals, and assuming that either is a homogeneous alloy within the probed depth or an epitaxial Ge overlayer, the Ge content in the surface is found to be about 35% at 500 °C and decreases to 20% at 600 °C. Otherwise, the peak near 55° in the XPD curve presents a significant shift (≈2.5°) at this temperature. This could be attributed to the fact that the epitaxial Ge film is under lateral compression because of the 4% lattice constant mismatch between Ge and Si. Indeed, Chambers and Loebs[17] successfully determined the strain at the lattice mismatch semiconductor heterojunctions Ge/Si(001) and Si/Ge(001) by examining x-ray-photoelectron diffraction features. But taking into account that the Ge lattice constant is larger than that of Si, this peak should be located at 53° and not at 57.5°, as observed. This means that lateral compression is not the cause of this 2.5° shift, but does not exclude the fact that the Ge film can be under strain. Furthermore, after exposure of this surface to 5.10^3-L atomic hydrogen, the (5×5) reconstruction disappears, as shown by LEED analysis (1×1 pattern), and the XPD curve in this case reveals no shift of the peak near 55°. Therefore, we believe that this could be due to the (5×5) surface reconstruction. Indeed, in analogy to the (7×7) surface reconstruction,[18] the atoms of the three topmost layers which are involved in the (5×5) surface reconstruction do not occupy the same positions as in the bulk. Basically, this should have an effect on the XPD phenomenon; this effect is not generally observed on thick film, but it is obvious that the thinner the film, the more important the surface reconstruction effect.

In addition, after annealing at 700 °C, the (5×5) pattern is completely replaced by a (7×7) pattern, and no mixing of the two patterns could be observed. This (7×7) pattern is absolutely the same as that obtained from a clean Si(111)7×7 surface. However, we believe that this 7×7 reconstruction does not proceed from a pure Si(111)7×7 surface, since ARUPS spectra were not quite the same as those obtained from a clean Si(111)7×7 surface. In particular, the location of the S_2 surface state in this case is about 0.1–0.2 eV lower in energy than in the case of the clean Si(111)7×7. At the same time, a change in the general profile of the XPD curve occurs. This suggests a change in the morphology of the film due to island formation or indiffusion of Ge into Si, which could be important at this range of temperature.

In the case of island formation, the (7×7) LEED pattern probably proceeds from a surface outside the island. Otherwise, the LEED diagram would result from the (7×7) reconstruction of a Si_xGe_{1-x} alloy at the surface. Assuming a homogeneous alloy, the Ge content is found to be about 15%. These results seem to be consistent with those of Märtensson *et al.*,[11] who reported that the 5×5 reconstruction was observed on surfaces with a Ge concentration estimated at 30–70% while the 7×7 reconstruction was observed on surfaces containing up to 24% of Ge. Moreover, we notice that similar observations and concentration have recently been reported in the case of Ge(111)-Sn(7×7) by Göthelid *et al.*[17]

Let us conclude by saying that our purpose was to investigate the structural changes of a Ge thin film deposited by LPCVD on a Si(111)7×7 surface as a function of the annealing temperature. The amorphous-crystalline transition was found to occur at an annealing temperature close to 400 °C and the 5×5 reconstruction of the Ge surface takes place at 500 °C. The Ge surface concentration was estimated to be about 35%. This 5×5 reconstruction appeared stable at annealing temperatures up to 600 °C, with a Ge surface concentration close to 20%. Moreover, the 5×5 reconstruction of the Ge thin film seemed to influence the XPD curve along the $[\bar{1}2\bar{1}]$ azimuthal direction; in particular, we could observe a 2.5° shift of the peak located near 55° along this direction. An annealing at 700 °C transformed the 5×5 reconstruction into a 7×7 reconstruction, which is the result of island formation or intermixing. In this case the Ge surface concentration was about 15%.

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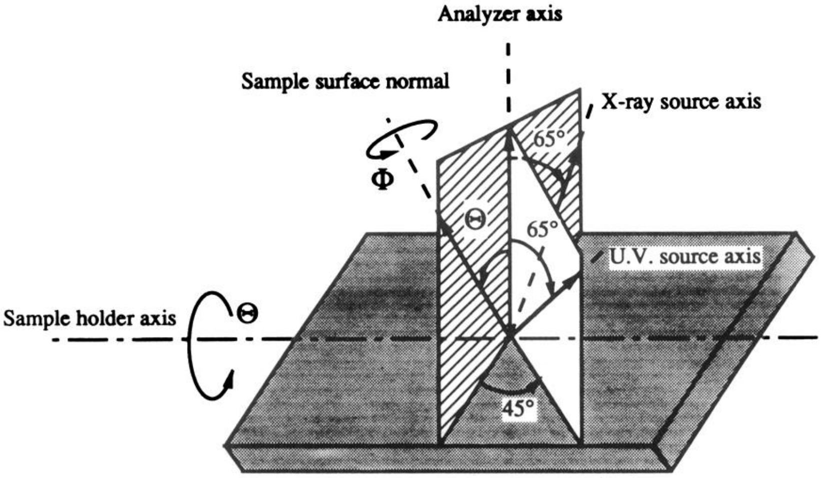

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