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Photoemission study of the thermal and catalytic decomposition of germane on a Si(111)7×7 surface

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Photoemission techniques have been used to discern the nature of the species involved in the adsorption of germane and catalytically decomposed germane on a Si(111)7×7 surface. It has been shown that the catalytic decomposition of germane induces—at very low substrate temperature (RT–300 °C)—in the Ge adsorption process, a mechanism quite different from the undecomposed germane adsorption. In this study, GeH, GeH_2, and GeH_3 radicals have been experimentally identified.

To further reduce the dimensions of electronic devices, many growth processes related to the chemical-vapor-deposition (CVD) technique have been proposed. Unfortunately, most of these techniques are currently not fully controlled and therefore, a better basic understanding of the CVD mechanism becomes necessary.

It is well known that the interaction of disilane with a Si(111)7×7 surface at room temperature (RT) leads to the formation of the SiH_2 dihydride phase, while the existence of the SiH_3 phase remains a matter of debate. Although SiH_2 and SiH species have been experimentally identified,[1–3] the photoemission study of adsorption of germane (GeH_4) on a Si(111)7×7 surface has never been reported as far as we know; no Ge hydride phase has been identified by photoemission analysis but a GeH monohydride phase (with a characteristic peak located at 4.9 eV below E_F).[4]

Our study is aimed at discerning the nature of the species involved in GeH_4 and catalytically decomposed GeH_4 (GeH_4^*) adsorption on a Si(111)7×7 surface at different substrate temperatures. For this purpose, we have investigated catalytic chemical-vapor deposition reported by Wiesmann *et al.*,[5] to obtain Ge films grown on a Si(111)7×7 surface. The gas source is germane (GeH_4). Catalytic decomposition of germane is expected to be very efficient for Ge deposition at very low substrate temperatures (room temperature–300 °C), which has already been observed in the case of Si deposition using disilane.[6]

The experimental procedure has been extensively described in Ref. 7. Silicon wafers (*p* type, 8×10 mm^2) were submitted to repetitive Ar^+ sputtering and 800 °C heating cycles, to achieve a clean surface. The surface cleanliness was checked by x-ray photoemission spectroscopy (XPS) and the 7×7 reconstruction by ultraviolet photoemission spectroscopy (UPS) [surface states at 0.2 (S_1), 0.8 (S_2), and 1.7 eV (S_3) below the Fermi level (E_F)].[8] 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 these experiments, no tungsten contamination of the studied samples has been detected by XPS techniques. The Si(111) samples could be heated by the Joule effect. A thermocouple fixed at the back of the wafer allowed substrate temperature measurements during heating. The substrate temperatures were also controlled by pyrometry. Exposures are expressed in langmuirs (1 L$=10^{-6}$ Torr s).

EXPERIMENT

Germane adsorption on a Si(111)7×7 surface

In these experiments, Si(111)7×7 samples were exposed to germane at different substrate temperatures. A 10^4-L exposure (10^4 Torr for 100 s) was used. The exposed samples were subsequently analyzed by UPS and XPS. UPS spectra are displayed on Fig. 1.

UPS spectrum in Fig. 1(a) is relevant to a clean Si(111)7×7 surface and shows three typical surface states located at 0.2 (S_1), 0.8 (S_2), and 1.8 eV (S_3) below E_F, while the UPS spectra 1*b*, 1*c*, and 1*d* belong to a Si(111)7×7 surface exposed to 10^4 L GeH_4 at room temperature, 300 °C, and 400 °C, respectively.

We first can note that the UPS spectrum 1*d* presents the same features as those of a clean Ge(111) *c*(2×8) surface and especially the two surface states located at 0.8 (S_1') and 1.4 eV (S_2') below E_F. These surface states are shown by Hamers, Tromp, and Demuth[8] to be specific to a Ge(111) *c*(2×8) surface. Thus we can believe that GeH_4 adsorption at this substrate temperature (400 °C) leads to a Ge thin film which is somewhat well ordered.

UPS difference spectra are also shown in order to reveal more explicitly different adsorbed species after a 10^4-L GeH_4 exposure.

Indeed, the UPS difference spectrum 1*f* (1*c* − 1*a*) clearly shows two peaks at 5.2 and 7.2 eV below E_F. These two peaks are characteristic of the presence of the SiH monohydride phase,[1] and have been experimentally identified in an earlier study of hydrogen adsorption on Si(111)7×7 surface.[2] XPS measurements have been performed and revealed in this case the presence of a very small quantity of germanium. We can also note that the vanishing (desorption or decomposition) of this phase has been achieved by an annealing at high temperature (≈400 °C). Thus, it is reasonable to believe that GeH_4 has been thermally decomposed at the 300 °C heated Si(111) surface. The atomic hydrogen which has resulted from this GeH_4 thermal decomposition may interact with the substrate surface to form SiH monohydride species.

At room temperature, as it is shown by the UPS

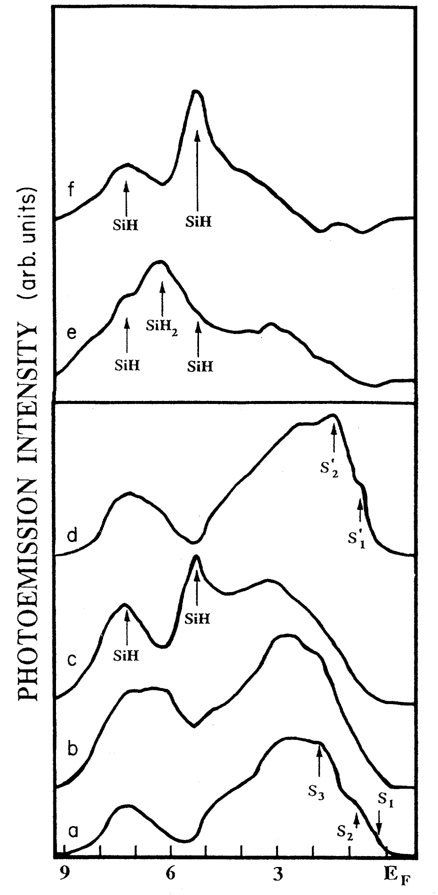

FIG. 1. UPS spectra of a Si(111)7×7 surface: *a*, clean; *b*, exposed to 10^4 L GeH$_4$ at RT; *c*, exposed to 10^4 L GeH$_4$ at 300 °C; *d*, exposed to 10^4 L GeH$_4$ at 400 °C; *e*, UPS difference spectrum (1*b* − 1*a*); *f*, UPS difference spectrum (1*c* − 1*a*).

difference spectra 1*e* (1*b* − 1*a*), the presence of the noticeable peak located at 6.2 eV below E_F reveals the formation of a SiH$_2$ dihydride phase. These species have also been detected by UPS techniques in the disilane adsorption on Si(111)7×7 surfaces at room temperature.[3] In addition, the SiH monohydride phase probably occurred as suggested by the presence of the peaks located at 7.2 and 5.2 eV below E_F. The very weak Ge 3*d* intensities in XPS measurements denote that a very small quantity of Ge is present in the analyzed samples (exposed at RT) as well as in the previous case (exposure to GeH$_4$ at 300 °C).

Catalytically decomposed germane (GeH$_4^*$) adsorption on a Si(111)7×7 surface

Our first experiment in this part of the study consisted in identifying the species which are adsorbed on a Si(111)7×7 surface after exposure to a 10^4-L catalytically decomposed germane at RT. After exposure, the sample was submitted to a succession of annealings at different temperatures to determine the desorption temperature of different species. UPS spectra are shown in Fig. 2. UPS spectrum 2*a* is relevant to a clean Si(111)7×7 surface, whereas 2*b* has been obtained after exposing a Si(111)7×7 surface to 10^4 L GeH$_4^*$ at RT. Spectra 2*c*, 2*d*, and 2*e* correspond respectively to the previously prepared thin film (2*b*) annealed at 80, 110, and 150 °C.

The difference spectra displayed in Fig. 2 would help to identify more clearly the different phases involved in GeH$_4^*$ adsorption. Indeed, the difference spectrum 2*f* (2*b* − 2*a*) obviously exhibits a large peak located at around 5.5 eV below E_F as well as a minimum near E_F (0.5 eV below E_F). According to the importance of its width, the peak located at around 5.5 eV below E_F is believed to correspond to more than one adsorbed species. Indeed, the difference spectra in Figs. 2*g*, 2*h*, and 2*i* show a minimum located at 5.9, 5.4, and 4.9 eV below E_F, respectively. There is no doubt that each of these minima is characteristic of the disappearance of an adsorbed species at the corresponding annealing temperature. Further-

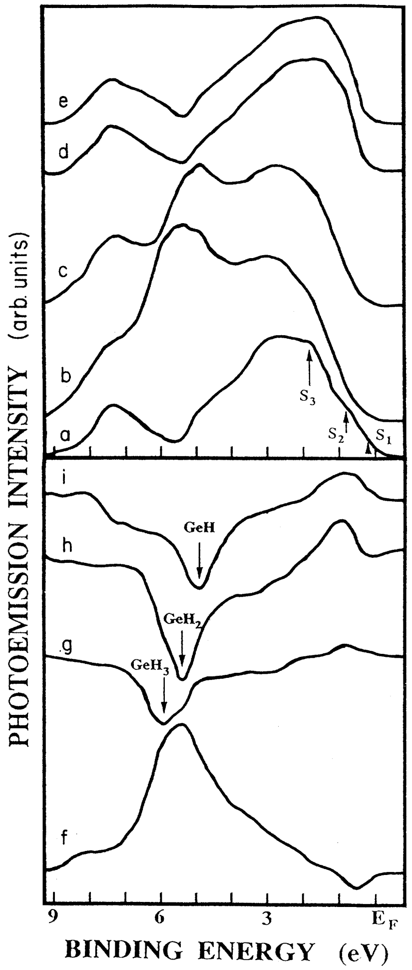

FIG. 2. UPS spectra of a Si(111)7×7 surface: *a*, clean; *b*, exposed to 10^4 L GeH$_4^*$ at RT; *c*, 2*b* plus annealing at 80 °C; *d*, 2*c* plus annealing at 110 °C; *e*, 2*d* plus annealing at 150 °C; *f*, UPS difference spectrum (2*b* − 2*a*); *g*, UPS difference spectrum (2*c* − 2*b*); *h*, UPS difference spectrum (2*d* − 2*c*); *i*, UPS difference spectrum (2*e* − 2*d*).

more, we can observe a peak located at 1 eV below E_F on both $2h$ and $2i$ difference spectra. A possible interpretation of these peaks and minima will be discussed in the next section. Moreover, it is interesting to note that XPS measurements have detected the presence of a quite noticeable quantity of Ge after an exposure to 10^4 L GeH_4^* at RT, whereas only a very small quantity of Ge is adsorbed when the gas source is not catalytically decomposed. After each annealing, no significant decreasing of the Ge $3d$ intensity has been observed. Using the well-known Beer-Lambert equation, and with the hypothesis of a Stranski-Krastanov growth, the deposited film is found to have a thickness of about 10 Å.

The UPS spectra corresponding to GeH_4^* adsorption on Si(111)7×7 at 200 °C ($3a$) and 400 °C ($3b$) are shown in Fig. 3. UPS spectrum $3a$ presents the same features as that of an amorphous Ge surface while UPS spectrum $3b$ could correspond to a monocyrstalline Ge(111) surface.

Moreover, in both cases [adsorption on Si(111)7×7 at 200 °C and 400 °C], XPS measurements exhibit a deposited Ge amount which is comparable to the case of Si(111)7×7 exposure to 10^4 L GeH_4^* at RT. A light shift (≈ 0.3 eV) of the Ge $3d$ core-level intensities has been detected between the two cases. This phenomenon has also been claimed by Patella *et al.*,[9] who observed a 0.25 eV shift of the Ge $3d$ core levels of amorphous as compared to crystalline Ge. So, according to these experiments, we can believe that a 10^4-L exposure to GeH_4^* at 200 °C of a Si(111)7×7 surface leads to the formation of an amorphous Ge film, while at a substrate temperature around 400 °C, the deposited film presents a crystalline structure, or nevertheless, a well-ordered structure. These results seem to be in agreement with those of Iyer *et al.*,[10] who observed, through Raman spectroscopy, that the crystallization of Ge occurred at around 220 °C.

Room-temperature atomic hydrogen adsorption on a Si(111)7×7 surface previously exposed to 10^4 L GeH_4^* at 400 °C

The deposited film obtained at 400 °C was then submitted to a 10^3-L atomic hydrogen exposure at RT (spectrum $3c$). Atomic hydrogen was produced by decomposing molecular hydrogen at a hot tungsten filament. As can be seen on the UPS difference spectrum $3d$ ($3c-3b$), the interaction of atomic hydrogen with the 400 °C deposited film has resulted in the presence of a peak located at 4.9 below E_F. This peak has been shown in an earlier study[4] to be specific of a GeH monohydride phase. Concurrently, a minimum located at around 0.5 eV below E_F appears. This corresponds to a valence-band maximum shift towards higher binding energies which reveals the saturation of all surface states.[4] It should be noted that a 10^3-L exposure to atomic hydrogen did not lead to surface contamination by species such as oxygen. Thermal decomposition of this monohydride phase has been achieved by annealing at a temperature above 150 °C, in agreement with Ref. 4. Then, the minimum located at 0.5 eV below E_F disappears, the surface states are relocated, and the UPS spectrum presents, again, the same features of a Ge film deposited at 400 °C or a monocrystalline Ge(111) sample.

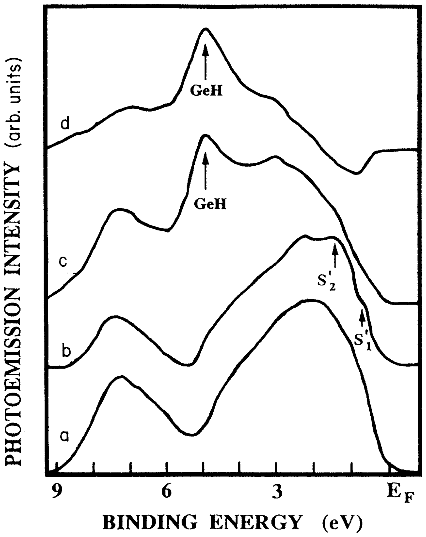

FIG. 3. UPS spectra of a, a Si(111)7×7 surface exposed to 10^4 L GeH_4^* at 200 °C; b, a Si(111)7×7 surface exposed to 10^4 L GeH_4^* at 400 °C; c, $3b$ plus exposure to 10^3-L atomic hydrogen; d, difference spectrum $3c-3b$.

DISCUSSION AND CONCLUSION

Our experiments on GeH_4 adsorption on Si(111)7×7 surface at around 300 °C clearly suggest the thermal decomposition of germane at the substrate surface which leads to the formation of a SiH monohydride phase (peaks located at 5.2 and 7.2 eV below E_F). Decomposition of this monohydride phase has been achieved by annealing the sample at around 450 °C. On the other hand, at RT, a 10^4-L exposure to GeH_4 of the Si(111)7×7 surface has resulted in the formation of other species which are SiH_2 (peak at 6.2 eV below E_F), in addition to the SiH monohydride phase (peaks at 5.2 and 7.2 eV below E_F). The coexistence of these two hydride phases has also been evidenced in RT decomposed disilane adsorption on Si(111)7×7 experiments.[3] In both cases (adsorption at RT and 300 °C), Ge $3d$ core-level measurements show the presence of a very small quantity of Ge, while at 400 °C, XPS measurements have detected a noticeable quantity of chemisorbed Ge (≈ 10 Å). Moreover, UPS spectrum of a sample prepared in this way denotes some order in the structure of the Ge deposited thin film. Similar results have been obtained by Kobayashi *et al.*,[11] who observed, by Laue reflection, a single crystallinity of Ge thin film deposited on Si(111) at 350 °C with low-pressure chemical-vapor-deposition techniques.

Catalytic decomposition of GeH_4 at a hot tungsten filament induced a quite different mechanism of the Ge film growth at substrate temperatures below 400 °C. Indeed, let us consider at first the case of GeH_4^* adsorption on a Si(111)7×7 surface at RT. The UPS spectra clearly show that the successive annealings have induced the disappearance of three species. The minimum located at 4.9 eV below E_F on the UPS difference spectrum $2i$ is obviously due to the disappearance of the GeH monohydride phase, according to its binding-energy position and to its desorption temperature. [GeH monohydride phase completely desorbs at 150 °C (Ref. 4).] Furthermore, as it has been previously shown, an annealing at a temperature around 110 °C leads to the disappearance of another species (minimum located around 5.4 eV below E_F on the UPS spectrum 2*h*). Because of the position of its binding energy, this species could not be any hydride phase of Si (SiH_2: 6.2 eV, desorption temperature $\approx 200\,^\circ C$; SiH: 5.2 and 7.2 eV, desorption temperature $\approx 450\,^\circ C$). It is strongly believed to be a hydride phase of Ge, and by analogy of the Si case, it is expected to be a GeH_2 dihydride phase (SiH_2 desorbs before SiH in the temperature range). At around 80 °C the disappearance of another species has been observed (minimum located at around 5.9 eV below E_F on the UPS difference spectrum 2*g*). As in the previous case, these species do not correspond to any previously identified species either. Comparing its desorption temperature and its binding energy to those of GeH_2 and GeH phases, the minimum could be logically attributed to a GeH_3 phase or to a physisorbed GeH_4 molecule desorption. Nevertheless, a photoemission study of GeH_4 condensation at very low temperature[12] (physisorbed case) has revealed a Ge 3*d* core-level shift towards higher binding energy (≈ 1 eV). This shift has not been observed in this experiment. Consequently, the minimum located at 5.9 eV below E_F is expected to correspond to the initially chemisorbed GeH_3 hydride phase. It could thus be imagined that the first chemisorbed species on a Si(111)7×7 surface exposed to 10^4 L GeH_4^* are only a GeH_3 hydride phase. This phase would be consequently decomposed into GeH_2 and maybe even GeH phases after an annealing at a temperature around 80 °C. In the same way, an annealing at a temperature around 110 °C could transform the GeH_2 dihydride phase into a GeH monohydride phase, which would be decomposed in Ge at a temperature around 150 °C. Nevertheless, the large peak located at around 5.5 eV below E_F on the UPS difference spectrum 2*f* supports the presence of more than one RT chemisorbed species before annealing. Furthermore, if GeH_3 was the only chemisorbed phase at RT, since the production of GeH_3 species would induce the production of atomic H which have higher sticking coefficient, a SiH phase should also be detected by UPS analysis. However, the presence of such a SiH phase has not been observed. Thus, catalytic decomposition of GeH_4 at a hot tungsten filament has probably produced GeH_3, GeH_2, and GeH radicals, which have higher sticking coefficient at RT than GeH_4. The higher growth rate obtained by the catalytic decomposition of germane could be explained by this phenomenon. Motooka and Greene[13] also admitted the presence of GeH_2 and GeH_3 radicals produced during the uv photolysis of GeH_4 in the uv laser-induced CVD. Moreover, we believed that a part of the observed GeH_2 species (annealing at 110 °C) has been provided by the thermal decomposition of GeH_3 at 80 °C which could explain the great quantity of this phase in comparison with the other two. Besides, the peaks located at 0.5 eV below E_F on the UPS difference spectra 2*h* and 2*i* are likely to correspond to the release of amorphous Ge surface states previously saturated by hydrogen (valence-band maximum shift towards higher binding energies).[14]

At a substrate temperature around 200 °C, a 10^4-L GeH_4^* exposure of a Si(111)7×7 surface leads to the formation of an amorphous Ge thin film with a thickness of about 10 Å. This amorphous Ge thin film could also be obtained by exposing a Si(111)7×7 surface to 10^4 L GeH_4^* at RT and subsequently annealing it at a temperature between 150 and 200 °C.

At a substrate temperature around 400 °C, a well-ordered deposited Ge thin film has been obtained by exposing a Si(111)7×7 surface to 10^4 L GeH_4^*, similar to the case where GeH_4 has not been catalytically decomposed. These results were expected, since the crystallization of Ge occurs at a temperature around 220 °C.[4,10] The deposition rates are comparable in both cases (exposure to GeH_4 and to GeH_4^*).

Atomic hydrogen adsorption at RT on a thin film, prepared at around 400 °C by exposing a Si(111)7×7 surface to 10^4 L GeH_4^* or GeH_4, has resulted in the formation of a GeH monohydride phase only, in accordance with the results of Ref. 10. Otherwise these results seem to be logical, since according to the vast majority of authors[15,16] a Stranski-Krastanov growth takes place with a two- to three-dimensional transition thickness of 3 monolayers without indiffusion. However, if indiffusion takes place at this temperature, as claimed by Ichikawa and Ino,[17] the topmost layer of the diffuse interface seems to be a Ge monolayer since no Si hydride phase, such as SiH or SiH_2 has been detected after exposure to 10^3-L atomic hydrogen at RT.

In summary, we have shown by photoemission techniques, the existence of GeH, GeH_2, and GeH_3 radicals, which are the result of the interaction of GeH_4^* with a Si(111)7×7 surface at RT.

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