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Comparative photoemission study of low-pressure hydrogen, silane, and disilane adsorption on Si(111)7×7

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We present an *in situ* study of low-pressure hydrogen, silane, and disilane chemisorption on Si(111) surfaces. Only characteristic signatures of mono- and dihydride phases are evidenced. At room-temperature sticking of SiH_2 or $(SiH_2)_n$ species for SiH_4 and Si_2H_6, respectively, are proposed and related to the back bonds of the dimer–adatom–stacking-fault model.

Chemical vapor deposition (CVD) is used throughout the microelectronic industry to deposit semiconducting and insulating thin films. When CVD is used to deposit silicon,[1] silicon oxides,[2] or silicon nitride,[3] monosilane is generally the gaseous silicon source. The use of disilane has recently been proposed to increase Si growth rates at low temperatures and to produce epitaxial layers of good crystalline quality.[4] Thermal cracking and adsorption of silanes on a Si(111) surface have until now been mainly studied by means of thermal desorption spectroscopy (TDS).[5] Only a few papers dealing with the nature of the chemisorbed species on Si(111) prepared under UHV conditions and analyzed by photoemission techniques are presently available.[6] In particular, the first stages of silane adsorptions as well as the thermal stability of the formed radicals with a Si(111) surface have only recently been investigated. As silane or disilane gases may also provide H radicals of much higher reactivity towards a Si surface than SiH_4 or Si_2H_6 molecules,[7] we first studied atomic hydrogen adsorption on the Si(111) surface. Photoemission spectra[8-12] obtained after hydrogen adsorption at about 350 °C are usually interpreted by the saturation of silicon dangling bonds (DB's) in agreement with theoretical results.[13-15] High-resolution spectroscopy[16-20] (HREELS) and infrared reflection[21] also conclude that a Si-H monohydride phase (i.e., one H atom bonded to every Si atom) occurs on all low-index silicon surfaces at elevated temperatures. For hydrogen adsorption at room temperature (RT), the coexistence of the monohydride and the dihydride (i.e., two H atoms bonded to every Si atom) phases at H saturation coverage is observed.[12,19]

In this work, we performed photoemission experiments to study the first stages of silane and disilane adsorption on the Si(111) surface. It will also be informative to look for similarities as well as for differences with results obtained on the Si(111)-H system.

EXPERIMENT

The experimental setup was extensively described elsewhere.[12] The samples were studied under ultrahigh vacuum conditions by ultraviolet (UPS) and x-ray (XPS) photoemission spectroscopies. The silicon samples (8×10 mm) were clamped on a tantalum sample holder and could be heated by joule effect. A thermocouple fixed at the back of the Si wafers allowed temperature measurements up to 1100 °C. Si(111) samples were treated in the usual way to achieve an ordered and clean surface (repetitive Ar^+ sputtering-heating cycles). The samples were considered clean before hydrogen, silane, or disilane adsorption when the XPS peak heights for impurities (C,O) were undetectable. The most sensitive probe for the surface cleanliness was the absence of bands due to O and water in the valence-band spectra obtained by UPS. Ultrapure gases were introduced into the UHV chamber through microleaks in order to control, accurately, pressure during exposure. During silane or disilane exposures, all filaments (ion gauges) were systematically turned off to avoid molecules cracking. In the experiments involving atomic hydrogen or dissociated disilane, dissociation is achieved at a hot tungsten filament, shielded and placed about 5 cm in front of the sample.

As the arrival rate for hydrogen, silane, or disilane gases was unknown we specify the H, SiH_4, or Si_2H_6 partial pressure times the exposure time ($1\ L = 10^{-6}$ Torr s).

A. Atomic hydrogen adsorption on Si(111)7×7

We exposed atomically clean Si(111)7×7 samples to H at various typical temperatures. Results are extensively exposed in Ref. 12.

Briefly, above 350 °C, UPS spectrum *b* of Fig. 1 exhibits exclusively characteristic peaks of the monohydride phase (5.3 and 7.3 eV below Fermi level E_F). We also display in Fig. 1 the difference spectrum $b-a$ (exposed spectrum minus clean spectrum) which clearly shows up the monohydride features. For a 10^3-L exposure we observe the vanishing of all surface states (SS) (S_1, S_2, and S_3, respectively, located at 0.35, 0.8, and 1.7 eV below E_F). Those SS are characteristic of the 7×7 surface reconstruction.[22] After a 10^3-L exposure at RT UPS spectrum *c* of Fig. 1 shows the coexistence of both monohydride and dihydride phases, the latter being characterized by a UPS feature located around 6.2 eV (below E_F). The coexistence of both phases is also clearly evidenced on the difference spectrum $c-a$ (Fig. 1). After

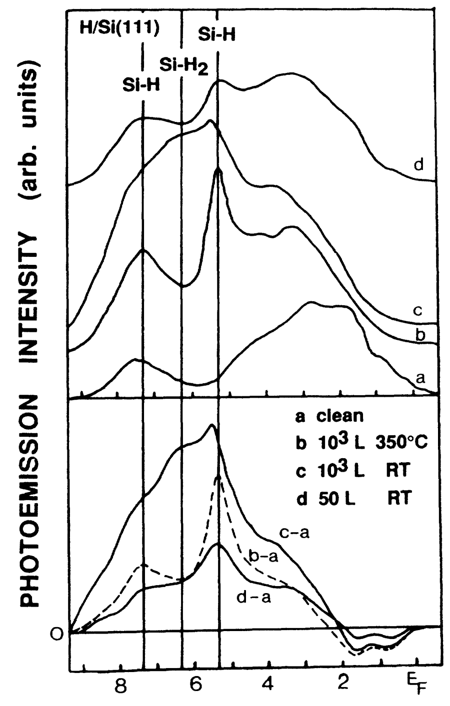

FIG. 1. UPS spectra and difference spectra for H exposures on Si(111)7×7.

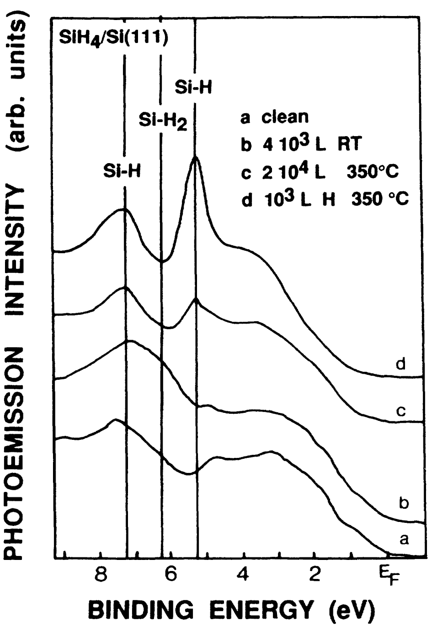

FIG. 2. UPS spectra and difference spectra for SiH_4 exposures on Si(111)7×7.

a low exposure (≈ 50 L) at RT the obtained spectrum *d* (Fig. 1) reveals the presence of a monohydride phase. In fact, all our photoemission experiments showed that during H exposure at RT a monohydride phase always appears before the dihydride phase. This particular point was probably overlooked in previous studies by the fact that at low H exposures water contamination results in the appearance of a marked feature located around 6.6 eV on UPS spectra.[23] Between RT and 250 °C we observe at H saturation (10^3 L) the coexistence of both mono- and dihydride phases. These phases progressively vanish as temperature increases. At around 550 °C no difference between clean and exposed surfaces can be observed.

B. Silane adsorption on Si(111)7×7

We exposed atomically clean Si(111)7×7 wafers at various significant temperatures with exposures ranging from a few langmuirs up to saturation. As shown in Fig. 2 the UPS spectrum *b* obtained after RT saturation (4×10^3 L) exhibits markedly a dihydride phase probably associated with a very weak monohydride phase. Surface states S_2 and S_3 are attenuated while S_1 is removed. The UPS spectrum of a clean Si(111)7×7 sample exposed at 350 °C to silane at saturation (2×10^4 L) exhibits exclusively the monohydride phase features [Fig. 2(c)]. The S_2 and S_3 surface states partially disappear while the S_1 state, related to the adatoms of the dimer-adatom-stacking-fault (DAS) model,[24] remains apparent. Independently of the exposure magnitude, XPS measurements revealed no significant shift of the Si 2*p* core level peak. After saturation of a Si(111)7×7 surface with silane at 350 °C we exposed it to a 10^3-L atomic hydrogen dose. This exposure corresponds to saturation of a Si(111)7×7 surface at 350 °C [Fig. 2(d)]. We observe an enhancement of the peaks associated to the monohydride phase whose intensity may be compared to an H-saturated Si(111) surface [Fig. 1(b)]. The vanishing of the S_1 surface state as well as a shift of the valence-band maximum to higher binding energies are observed. If we compare magnitudes of the feature located at 5.3 eV after silane saturation [Fig. 2(c)] or H saturation [Fig. 2(d)], we get a ratio of about 1/3. Finally, a 550 °C anneal totally desorbs the Si-H phase inducing the recovery of the surface states S_1, S_2, and S_3 of the Si(111)7×7 surface.

C. Disilane adsorption on Si(111)7×7

Figure 3 summarizes the UPS data for Si_2H_6 adsorbed at RT on Si(111)7×7 as a function of exposure. In all experiments, even for low exposures [Figs. 3(a) and 3(b)] we only observe the characteristic feature of the dihydride phase. Figure 3 also displays the difference spectra between exposed and clean surfaces. A spectrum of a hydrogenated Si(111) surface is shown (spectrum *e*) for comparison. Spectra *d* and *e* are obtained after a same 10^4-L exposure of disilane or H, respectively. All surface states are removed in both cases. The important SiH_2 peak suggests the formation of an amorphous $(SiH_2)_n$ network. Figure 4 shows some UPS spectra obtained after various exposures of a Si(111)7×7 surface to disilane 350 °C. Associated difference spectra (exposed spectrum minus

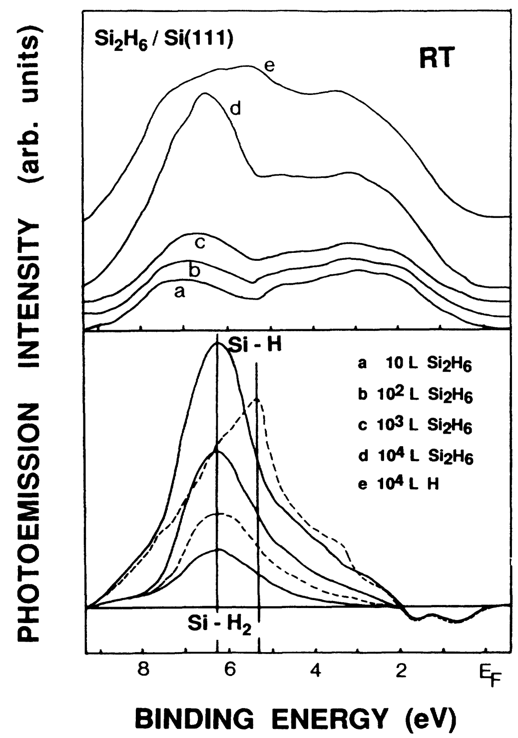

FIG. 3. UPS spectra and difference spectra for Si_2H_6 on Si(111)7×7 at RT.

clean spectrum) are also presented. Spectra *d* and *e* are obtained after a same 10^4-L saturation coverage of disilane or H, respectively. Only the characteristic monohydride phase is observed. It is worth noting that the magnitude of the 5.3-eV feature induced by disilane [Fig. 4(d)] is weaker than that obtained after H saturation [Fig. 4(e)]. All surface states are not removed after disilane exposures in contrast with H adsorption. After disilane exposure in the (RT, 350 °C) temperature range we observe the coexistence of both mono- and dihydride phases. Disilane adsorption on Si(111) induces no significant shift of the Si 2*p* core level. A 550 °C anneal totally desorbs the Si-H phase inducing the recovery of the surface states S_1, S_2, and S_3 of the Si(111)7×7 surface.

As already observed by Imbihl *et al.*,[25] previously hydrogenated silicon surfaces are inactive towards RT disilane chemisorption. A silicon surface previously saturated with monohydride phase does not accordingly adsorb disilane at RT.

DISCUSSION

Only the mono- and dihydride phases were observed in all our experiments. Our results are in full agreement with previously published UPS spectra characteristic of the mono- and dihydride phases. A trihydride phase has been envisaged both theoretically and experimentally.[26] However, its existence is still controversial,[19] and up to now there has been no well-admitted UPS signature corresponding to such a phase. Even if such a trihydride phase were present, its weak magnitude would make it hardly detectable by photoemission techniques.[27] There is no evidence from our XPS results of a possible silicon deposit from the low-pressure silane gas phase on the Si(111)7×7 surface. However, our UPS results show that silicon deposition occurs. Experimental evidence for silicon deposition as observed with photoemission spectroscopies is as follows:

(a) Experimental results obtained with silane at 350 °C are different from those obtained with hydrogen. After silane saturation the magnitude of the 5.3-eV Si-H feature is only about $\frac{1}{3}$ of that obtained in the same conditions with hydrogen. The S_1 surface state is still present whereas S_2 and S_3 are strongly attenuated. One may presume that Si-H groups stick atop of the rest atoms of the DAS model. Similar conclusions were inferred for the growth of the Ge/Si(111)7×7 interface.[28] During hydrogen adsorption at 350 °C H atoms occupy all surface sites (vanishing of all surface states). Rest atoms only represent $\frac{1}{3}$ of the available sites (six rest atoms out of the nineteen dangling bonds in each unit cell of the DAS model[22]).

(b) For disilane, the presence of an important dihydride phase at RT with no associated monohydride phase is a notable difference when compared to hydrogen adsorption on Si(111)7×7.

What radicals could be invoked to explain the observed phases? Our results on the hydrogen chemisorption on Si(111)7×7 indicate unambiguously that (i) atomic hydrogen has a higher sticking coefficient than silane or disilane. (ii) A monohydride phase forms first at RT for very

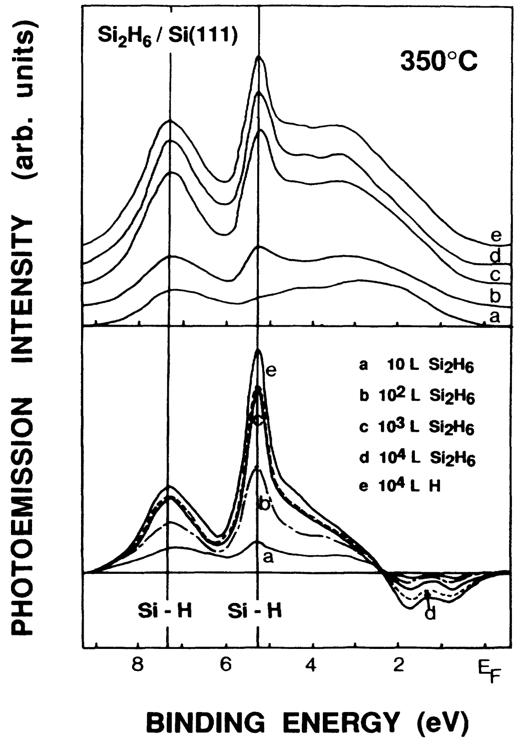

FIG. 4. UPS spectra and difference spectra for Si_2H_6 exposures on Si(111)7×7 at 350 °C.

low H exposures.

During *silane* exposure at RT, the main species detected by our mass spectrometer were SiH_2 radicals and at saturation we observe essentially a dihydride phase. In the unit cell of the Si(111)7×7 surface, the available DB's are located on adatoms and rest atoms with a distance of around 7 Å between two adatoms and around 4.5 Å between an adatom and a rest atom. SiH_2 groups need two dangling bonds to stick on the Si surface. A possibility which agrees well with the observed partial vanishing of surface states is a DB for an adatom or rest atom and a defect in the vicinity. A Si(111)7×7 surface is not as rough as a Si(100)2×1 surface when observed by STM. However, the Si(111)7×7 surface will exhibit enough defects[29] to support the idea suggested above. This could explain the low sticking coefficient of SiH_4 on this surface. Another argument is the comparable sticking coefficient of monosilane and disilane on an amorphized silicon surface[30] on which many DB's are available.

After RT *disilane* adsorption we observe a strong dihydride phase exclusively without an associated monohydride phase. This observation rules out the formation of H at the surface. To explain that important dihydride phase which does not saturate even after high disilane exposure, we suggest sticking of the $(SiH_2)_n$ species. Such a $H_2Si\text{-}SiH_2$ group requires two DB's to stick on the surface and the distance between these two bonds[31] is close to the adatom-rest-atom distance mentioned above. The thermodynamic stability of the Si—Si bond is weak as compared with the Si—H bond and its breaking allows adsorption of a new $(SiH_2)_2$ group.[32] This explains the formation of an important dihydride phase at RT similar to that observed on an amorphized Si surface. The gas-phase pyrolysis mechanism of disilane supports the formation of $Si\text{-}H_2$ groups.[31] However, as $Si\text{-}H_2$ groups have a very low sticking coefficient (see silane adsorption discussed above), their contribution to the dihydride phase during disilane adsorption is negligible. By annealing the dihydride phase transforms totally into a Si-H phase as already observed by TDS.[25]

At higher temperature, the monohydride phase can be formed from Si_xH_y fragments or H atoms. A Si(111) surface saturated with a Si-H phase cannot accordingly chemisorb disilane molecules as no bonds with adequate conformation are available.

To summarize, our results indicate that on the Si(111) surface the observed dihydride phase can be formed by sticking of atomic hydrogen and/or $(SiH_2)_n$ groups. Similar results are probably obtained on other low-index Si surfaces or even on amorphous Si.

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[1] W. A. P. Claasen, J. Bloem, W. G. J. N. Valkenburg, and C. H. J. van den Brekel, J. Cryst. Growth **57**, 259 (1982).

[2] M. L. Hitchman and A. E. Widmer, J. Cryst. Growth **55**, 501 (1981).

[3] S. Hasegawa, M. Matuma, H. Anbutu, and Y. Kurata, Philos. Mag. B **56**, 633 (1987).

[4] H. Hirayama, T. Tatsumi, and N. Aizaki, Appl. Phys. Lett. **18**, 52 (1988).

[5] S. M. Gates, Surf. Sci. **195**, 307 (1988), and references therein.

[6] D. Muller, F. Ringeisen, D. Bolmont, and J. J. Koulmann, Surf. Sci. **211/212**, 986 (1989).

[7] M. Alaoui, F. Ringeisen, D. Bolmont, and J. J. Koulmann, in *Proceedings of the European Materials Research Society Third International Symposium on Si Molecular-Beam Epitaxy, Strasbourg, 1989* [Thin Solid Films (to be published)].

[8] H. Ibach and J. E. Rowe, Surf. Sci. **43**, 481 (1974).

[9] T. Sakurai and H. D. Hagstrum, Phys. Rev. B **12**, 5349 (1975).

[10] T. Sakurai and H. D. Hagstrum, Phys. Rev. B **14**, 1593 (1976).

[11] T. Sakurai and H. D. Hagstrum, J. Vac. Sci. Technol. **13**, 807 (1976).

[12] D. Muller, F. Ringeisen, J. J. Koulmann, and D. Bolmont, Surf. Sci. **189/190**, 472 (1987).

[13] J. A. Applebaum and D. P. Hamman, Phys. Rev. Lett. **34**, 806 (1975).

[14] K. C. Pandey, Phys. Rev. B **14**, 1557 (1976).

[15] K. M. Ho, M. Schlüter, and M. L. Cohen, Phys. Rev. B **15**, 3888 (1977).

[16] H. Wagner, R. Butz, U. Backes, and D. Bruchmann, Solid State Commun. **38**, 1155 (1981).

[17] F. Stucki, J. A. Schaefer, J. R. Anderson, G. J. Lapeyre, and W. Göpel, Solid State Commun. **47**, 795 (1983).

[18] H. Kobayashi, K. Edamoto, M. Onchi, and M. Nishijima, J. Chem. Phys. **78**, 7429 (1983).

[19] R. Butz, E. M. Oellig, H. Ibach, and H. Wagner, Surf. Sci. **147**, 343 (1984).

[20] H. Froitzheim, U. Köhler, and H. Lammering, Surf. Sci. **149**, 537 (1985).

[21] Y. J. Chabal, E. E. Chaban, and S. B. Christman, J. Electron. Spectrosc. Relat. Phenom. **29**, 35 (1983).

[22] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).

[23] W. Ranke and D. Schmeisser, Surf. Sci. **149**, 485 (1985).

[24] K. Takayanagi, T. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).

[25] R. Imbihl, J. E. Demuth, S. M. Gates, and B. A. Scott, Phys. Rev. B **39**, 5222 (1989).

[26] K. C. Pandey, T. Sakurai, and H. D. Hagstrum, Phys. Rev. Lett. **35**, 1728 (1975).

[27] S. Veprek, F. A. Sarrott, S. Rambert, and E. Taglauer, J. Vac. Sci. Technol. A **7**, 2614 (1989).

[28] B. N. Dev, G. Materlik, F. Grey, R. L. Johnson, and M. Clausnitzer, Phys. Rev. Lett. **57**, 3058 (1986).

[29] F. M. Leibsle, A. Samsavar, and T. C. Chiang, Phys. Rev. B **38**, 5780 (1988).

[30] J. J. Koulmann, F. Ringeisen, M. Alaoui, and D. Bolmont (unpublished).

[31] *Gmelin Handbook of Inorganic Chemistry, Silicon,* 8th ed. (Springer-Verlag, Berlin, 1982).

[32] J. J. Koulmann, D. Muller, F. Ringeisen, and D. Bolmont, Phys. Rev. B **39**, 8768 (1989).