RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 12 15 APRIL 1989-II

Broken-dimer model in a-Si:H

J. J. Koulmann, D. Muller, F. Ringeisen, and D. Bolmont
Laboratoire de Physique et de Spectroscopie Electronique, Faculté des Sciences et Techniques, Université de Haute-Alsace,
4 rue des Frères Lumière, 68093 Mulhouse CEDEX, France

(Received 19 January 1989)

We present an *in situ* study of hydrogen chemisorption on amorphized silicon wafers. Evidence is presented through ultraviolet photoemission spectroscopy for reversible dihydride phase formation at temperatures below 470 K. A model of broken dimers in metastable thermal equilibrium with hydrogen explains many observed properties of a-Si:H.

The wealth of experimental data published during the past years does not yield a consensus about the nature of the gap states in hydrogenated amorphous silicon (a-Si:H). The interest in the subject has been heightened as more refined experimental methods yield more conflicting results. As possible defects, only threefold-coordinated atoms known as dangling bonds (D centers) and complexes made up of D centers have been considered. The density of these centers is reduced by hydrogenation through formation of Si—H bonds and that H evolution occurs through breaking of these bonds.[1] The properties of a-Si:H are a direct consequence of the deposition process, notably the visible microstructure[2] but only few results on the microscopic structure of these materials are available. The most common picture represents D centers pointing into a microvoid or residing on an internal surface with all the atoms on the front side being fourfold coordinated. These voids are embedded in a undefined distorted Si network. To shed some light on the structure of hydrogen in these voids, we carried out a photoemission study of the behavior of hydrogen toward an amorphized silicon surface. Previous results[3] showed that such an amorphized surface is a good representation of a-Si internal surface.

The experimental procedure is largely exposed in Ref. 3. Briefly, Si(111) and Si(100) wafers were submitted to repetitive (Ar^+ sputtering-heating) cycles to clean the surface. All samples were then amorphized by Ar^+-ion sputtering to achieve a disordered surface. The samples are studied through ultraviolet photoemission spectroscopy (UPS). Recorded UPS spectra of the obtained amorphized silicon surfaces are identical to those obtained on a-Si by von Roedern.[4,5]

After cleaning, the amorphized silicon wafers were exposed to a monoatomic H pressure (10^{-5}–10^{-6} Torr) for a given time. Atomic hydrogen was produced in the usual way by dissociation of ultrapure H_2 on a hot W filament. H^+-species production can thus be stopped at once by turning the dissociation filament off.

After exposure of our atomically clean amorphized Si surface at 600 K to atomic H for exposures in the range 100–1000 L (1 Langmuir $= 10^{-6}$ Torr×1 s), UPS difference spectra (i.e., exposed spectrum − clean spectrum) of Fig. 1 reveal the Si-H characteristic peak (5.3 eV below E_F).[6] The dip located at 0.7 eV below E_F corresponds to the 0.7-eV valence-band-maximum (VBM) shift toward higher binding energies. That VBM shift is relevant to the vanishing of the π_b dangling-bond (DB) states observed on Si(100)-2×1:H surface (monohydride form only).[7]

When atomically clean amorphized silicon wafers are exposed to atomic H at room temperature (RT), UPS spectra shown in Fig. 2 reveal two different steps in the H adsorption process. Below 50 L [Fig. 2(a)], we observe only monohydride phase formation. At higher exposures [Fig. 2(b)], a polyhydride phase grows as confirmed by the appearance of a 5.6-eV contribution shifting progressively toward higher binding energies when H doses increase, finally fixing around 6 eV after H saturation (1000 L). In fact, the growth of the Si-H_2 peak (6.2 eV below E_F) (Ref. 5) superimposes on the already formed monohydride peak (5.3 eV) and causes an apparent shift of the hump resulting from their superposition.

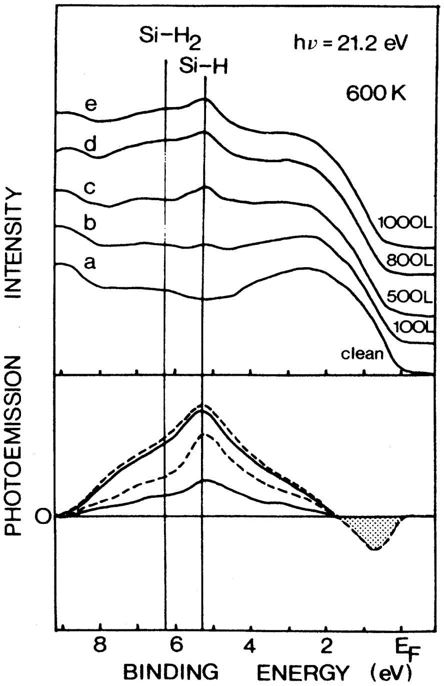

FIG. 1. UPS spectra and difference spectra for H exposures at 600 K. a, clean; b, 100 L; c, 500 L; d, 800 L; and e, 1000 L.

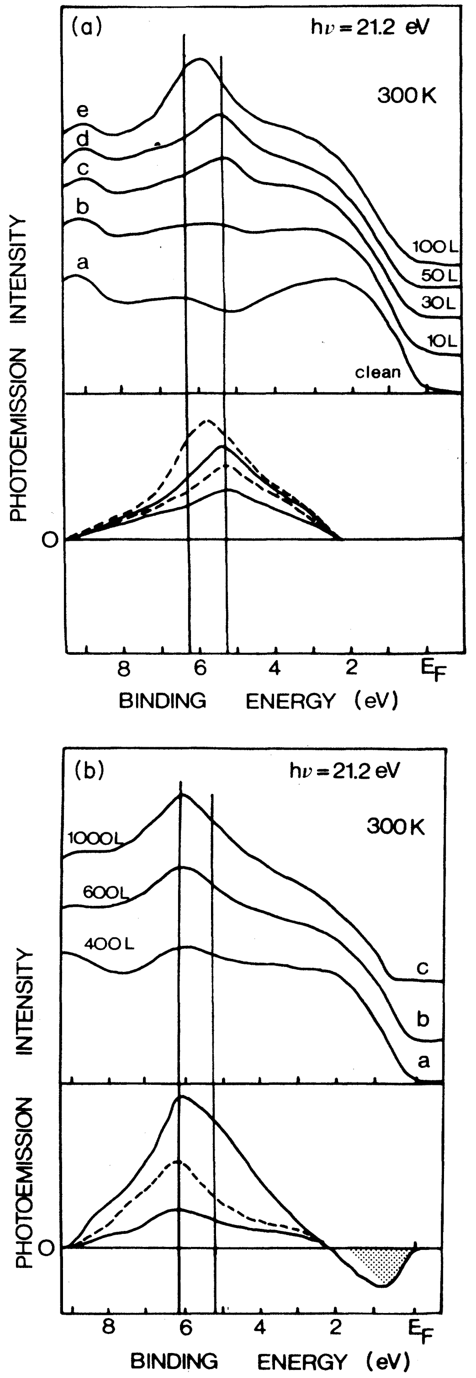

FIG. 2. (a) UPS spectra and difference spectra for H exposures at 300 K. Spectrum *a*, clean; *b*, 10 L; *c*, 30 L; *d*, 50 L; and *e*, 100 L. (b) UPS spectra and difference spectra for H exposures at 300 K. Spectrum *a*, 400 L; *b*, 600 L; and *c*, 1000 L.

As for high-temperature exposures, dangling-bond states progressively disappear when *H* doses increase as illustrated by the wide dip at about 0.7 eV below E_F. That dip is broader [1.4 eV full width at half maximum (FWHM)] for RT exposure at saturation as that obtained at 600 K (0.9 eV FWHM) in the same exposure conditions. We conclude that all DB's (or other bonds?) are not quenched by the monohydride form. A surface state (around 1.8 eV below E_F) attributed to dimer bonds and still present on the monohydride surface disappears with the growth of the dihydride phase on the Si(100)-1 × 1:2H system.[8]

Further, we investigated the influence of substrate temperature (in the range 300 to 600 K) on the existence of that dihydride phase. UPS spectra are recorded when H saturation is achieved (1000 L). As shown (Fig. 3) by UPS difference spectra, the dihydride phase is strongly attenuated around 420 K, disappearing around 470 K. Similar evolution is observed after anneal of a hydrogen saturated surface prepared at RT and subsequently heated to temperatures in the range 300 to 600 K. For any temperature between 300 and 600 K, thermal desorption or adsorption in saturating conditions yields identical UPS spectra (Fig. 4).

In another experiment (Fig. 5), we first saturated a clean *a*-Si surface with atomic H at 600 K to give existence to a stable monohydride phase (spectrum *a*). The obtained surface is then submitted at RT to a 800-L H exposure inducing a Si-H_2 dihydride phase superimposing to the already formed Si-H phase which remains unaffected (spectrum *b*). In that configuration, monohydride and dihydride phases coexist. However, when heating takes place (≈ 600 K), Si-H_2 phase desorption occurs leaving the Si-H phase alone and unaltered (spectrum *c*).

When a new RT hydrogenation is carried out (800 L),

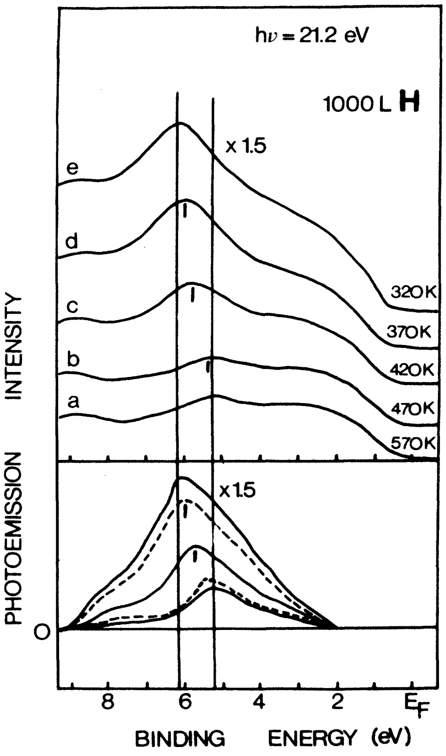

FIG. 3. UPS spectra and difference spectra after 1000-L H exposure at different substrate temperatures *a*, 570 K; *b*, 470 K; *c*, 420 K; *d*, 370 K; and *e*, 320 K.

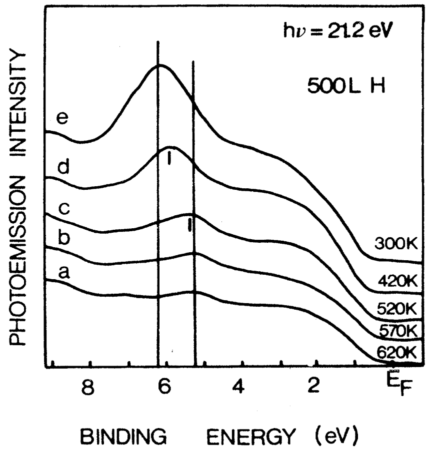

FIG. 4. UPS spectra after 500 L H exposure at RT (spectrum *e*) and subsequent annealing at *a*, 620 K; *b*, 570 K; *c*, 520 K; and *d*, 420 K.

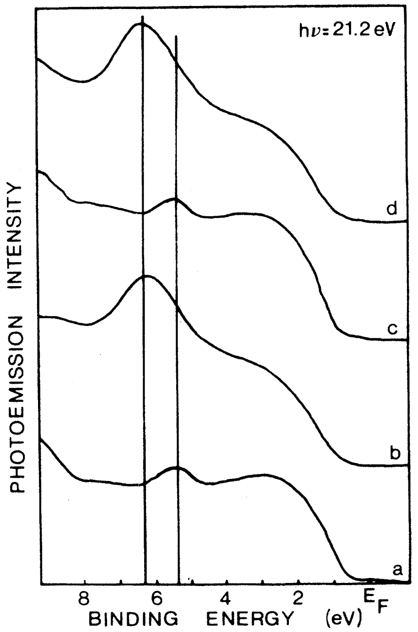

FIG. 5. UPS spectra illustrating the Si-H_2 formation ↔ Si-H_2 desorption reversibility: *a*, H-saturated (1000 L) amorphized Si surface at 600 K: monohydride phase appears; *b*, addition RT H exposure (+800 L): dihydride phase appears; *c*, by heating (600 K) dihydride phase desorbs while monohydride phase remains alone and unaffected; and *d*, after addition RT H exposure, dihydride phase reappears.

dihydride phase reappears (spectrum *d*). Repetitive Si-H_2 formation (by RT hydrogenation) and Si-H_2 desorption (by heating) can be performed without affecting the monohydride phase. This reversibility was also evidenced for any lower substrate temperature in the range 300 to 450 K.

This low-temperature reversibility requires a weak bond already invoked by several workers to explain their results.[9-11] A Si-Si dimer[12] could be a good candidate for such a weak bond. Such dimers may be formed by closely spaced Si atoms and may after breaking present two dangling bonds per Si atom at the surface. The basic dimer model for the low-density Si(100) orientation was recently confirmed by scanning tunneling microscopy studies.[13] The low-temperature reversibility induced by that dimer configuration could be a means for a better understanding of *a*-Si:H materials. In RT deposition conditions, dimer bonding is the most important configuration present in the material. By breaking of dimers, two dangling bonds become available to H adsorption as compared with the threefold coordinated Si with only one bond available for H. This explains why H concentrations up to 50% are observed[1] and why ir measurements[14] show a large predominance of dihydride phase. This leads to a porous material as visualized by scanning electron microscopy.

Higher substrate temperatures (520 K) produces a more compact *a*-Si:H material containing essentially Si-H (Ref. 14) groups and induces an *a*-Si network with few visible defects but a higher concentration of *D* centers.

At intermediate temperatures we observe a more complex situation where porous domains are embedded in a compact *a*-Si network. These porous domains are essentially made of voids containing more H than needed[15] to maintain thermal equilibrium with broken dimers located on the internal surface. The result is a metastable structure usually associated with melt-cooled glasses. The temperature for glass transition (around 400 K) (Ref. 16) corresponds to the strong decrease of the dihydride phase. When equilibrium is reached, coexistence between Si-H and Si-H_2 phases is observed.[14] After annealing in the temperature range 300 to 500 K, hydrogen effuses partially out of the voids and equilibrium is broken. Dimers form again with corresponding Si-H_2 phase decrease, the monohydride phase remaining nearly unaffected.[17-19] As long as H has not totally effused out from the voids (depending on annealing temperature and time) the broken dimer reversibility can partially restore the previous dihydride phase[20] at temperature below 420 K. After long annealing at around 600 K the hydrogen departure occurs with the breaking of the dihydride phase and the equilibrium is definitively destroyed. The possibility that broken dimer bonds accept other elements than H (as, for example, F, Cl, dopants or SiH_x groups[21]) cannot be rejected. This broken dimer model could provide a possible frame to explain other observed properties related to reversibility as for example in the Staebler-Wronski effect[22] or in thermal-induced hydrogen diffusion.[23]

In summary we find that structure and properties of *a*-Si:H are correctly described by our H ↔ broken-dimer model without excluding other possible corrections as for example floating bonds[19] to explain partially the mechanism of H effusion.

[1] See, e.g., *The Physics of Hydrogenated Amorphous Silicon,* edited by J. D. Joannopoulos and G. Lucovsky (Springer-Verlag, New York, 1984).

[2] J. C. Knights and R. A. Lujan, Appl. Phys. Lett. **35**, 244 (1979).

[3] D. Muller, F. Ringeisen, D. Bolmont, and J. J. Koulmann, J. Non-Cryst. Solids **97 & 98**, 1411 (1987).

[4] B. von Roedern, L. Ley, and M. Cardona, Phys. Rev. Lett. **39**, 1576 (1977).

[5] L. Ley, in *Photoelectron Emission Studies in Semiconductors and Semimetals,* edited by J. J. Pankove (Academic, Orlando, 1984), Vol. 21, pp. 385–426.

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

[7] R. J. Hamers, Ph. Avouris, and F. Bozso, J. Vac. Sci. Technol. A **6**, 508 (1988).

[8] R. I. G. Uhrberg, L. S. O. Johansson, and G. V. Hansson, in *The Structure of Surfaces II,* edited by J. F. van der Veen and M. A. van Hove, Springer Series in Surface Sciences, Vol. 11 (Springer-Verlag, Amsterdam, 1987), p. 303.

[9] K. Zellama, P. Germain, S. Squelard, B. Bourdon, J. Fontenille, and R. Danielou, Phys. Rev. B **23**, 6648 (1981).

[10] H. J. Clemens, Solid State Commun. **51**, 483 (1984).

[11] M. Stutzmann, W. B. Jackson, and C. C. Tsai, Phys. Rev. B **32**, 23 (1985).

[12] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[13] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[14] M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).

[15] Y. J. Chabal and C. K. N. Patel, Phys. Rev. Lett. **53**, 210 (1984).

[16] R. A. Street, J. Kakalias, and T. M. Hayes, Phys. Rev. B **34**, 3030 (1986).

[17] D. K. Biegelsen, R. A. Street, C. C. Tsai, and J. C. Knights, Phys. Rev. B **20**, 4839 (1979).

[18] M. Kumeda and T. Shimizu, Jpn. J. Appl. Phys. **19**, L197 (1980).

[19] S. T. Pantelides, Phys. Rev. Lett. **58**, 1344 (1987).

[20] R. Tsu, D. Martin, J. Gonzalez-Hernandez, and S. R. Ovshinsky, Phys. Rev. B **35**, 2385 (1987).

[21] D. Muller, F. Ringeisen, D. Bolmont, and J. J. Koulmann, Surf. Sci. (to be published).

[22] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).

[23] W. Beyer, in *Tetrahedrally-Bonded Amorphous Semiconductors,* edited by David Adler and Hellmut Fritzsche (Plenum, New York, 1985).