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Quantum size effects on the optical band gap of microcrystalline Si:H

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We have succeeded in fabricating the mostly crystallized Si:H materials having a wide optical band gap of up to 2.4 eV by means of a reactive sputtering technique with a low substrate temperature of ~100 K. The structural analysis showed that the materials consist of small crystalline silicon particles surrounded by hydrogen atoms, whose diameters are 20–30 Å. The widening of the optical band gap can be explained by a three-dimensional quantum-well effect in the small particles.

The optical band gap of the binary Si:H materials increases almost linearly with increasing hydrogen content[1] and the result is explained by the simple alloying effect. However, some of the previous data cannot be explained by the hydrogen content alone. For example, the Si:H material prepared by the homogeneous chemical vapor deposition of SiH_4 has an optical band gap of 2.55 eV at a hydrogen content of 40 at.%,[2] whereas the material prepared by the plasma chemical vapor deposition of Si_2H_6 has that of 2.05 eV at the same hydrogen content.[3,4] The discrepancy in the two optical band gaps is very large. Therefore, some other effects as well as the hydrogen content strongly affect the optical band gap. On the other hand, a one-dimensional quantum size effect on the optical band gap has been shown using hydrogenated amorphous silicon (a-Si:H)/a-SiN_x:H superlattices,[5] in which the quantum wells are intentionally formed. The optical properties, such as the optical band gap, of the superlattices are, however, between those of a-Si:H and a-SiN_x:H, so that some undesirable effects, such as the interdiffusion of the nitrogen atoms, cannot be excluded.

In this paper, we show the evidence for the quantum size effect in the silicon-based materials. The mostly crystallized binary Si:H materials are prepared in order to confirm the structure, and in order to exclude the ambiguity arising from the disorder and the interdiffusion. The optical band gaps of the obtained materials are very large (up to 2.4 eV), even though they are mostly crystallized. The values are quite different from those of conventional microcrystalline Si:H.[6,7] Based on the structural analysis and the simplified calculation, the widening of the optical band gap can be explained by a three-dimensional quantum-well effect.

The materials used in this study are fabricated by means of a planar magnetron rf sputtering technique in hydrogen gas onto a low temperature (~100 K) substrate. In the sputtering chamber, the substrate was held on the 5-cm-diam upper electrode. The lower electrode buried by permanent magnets holds the silicon disk target of a 7.5 cm diameter. The distance between these electrodes is 4.5 cm. In order to change the material properties, the rf power and hydrogen gas (99.999 99% purity) pressure were varied from 50 to 300 W and from 0.2 to 2 Torr, respectively. The material was 1—15 μm thick, and was deposited on fused quartz and single-crystal silicon substrates. The materials on fused quartz substrates were observed by optical absorption (0.2—0.9 μm) and Raman scattering. The materials on single-crystal silicon substrates were observed by infrared absorption (2.5—25 μm) and x-ray diffraction. In the x-ray diffraction measurements, the incident beam angle was held constant at 7°, and the detector was scanned from 5 to 80°, which were measured from the incident beam direction. These configurations cause an increase in the diffracted beam intensity from the Si:H materials, and suppress the signal from single-crystal silicon substrates.

Figure 1 shows the relationship between optical band gap and hydrogen content. The optical band gap was determined by $(\alpha\hbar\omega)^{1/2}$-vs-$\hbar\omega$ measurements, where α and $\hbar\omega$ are the absorption coefficient and the photon energy, respectively (see inset in Fig. 1). The hydrogen content was deduced from the integration of the infrared absorption band due to Si—H stretching vibrations, which

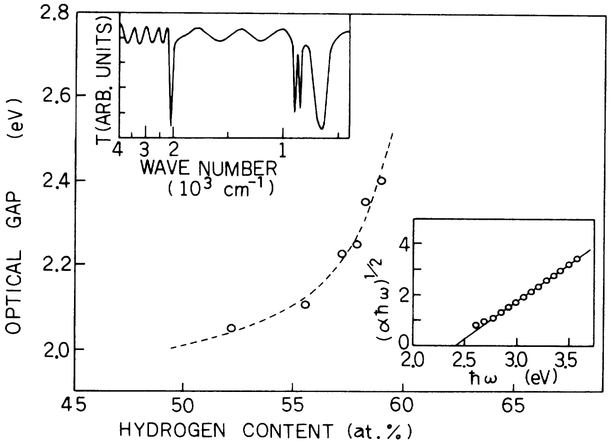

FIG. 1. Optical band gap vs hydrogen content. Upper inset shows typical infrared absorption spectrum for the present materials (T: transmittance). Lower inset shows typical $(\alpha\hbar\omega)^{1/2}$-vs-$\hbar\omega$ plots, from which optical band gaps are determined [$(\alpha\hbar\omega)^{1/2}$: in units of 10^2 $cm^{-1/2}$ $eV^{1/2}$].

appears near 2100 cm^{-1} (see inset in Fig. 1).[8] In order to obtain an accurate hydrogen content, the interference effect appeared in the infrared absorption spectrum also taken into account. As shown in Fig. 1, the optical band gaps of the present materials are greater than those of conventional a-Si:H by about 0.3–0.6 eV. (The films are transparent, and the color is pale yellow.)

The Si—H bond configuration can be estimated from the infrared absorption spectrum. It shows strong absorption bands near 850 and 890 cm^{-1}, suggesting the presence of $(\mathrm{SiH}_2)_n$ ($n \geq 1$) or SiH_3 groups.[3,4,8,9] Taking into account the stretching absorption wave number (2090–2100 cm^{-1}), we conclude that the hydrogen atoms are incorporated in the form of $(\mathrm{SiH}_2)_n$ ($n=1$ or 2).[3,4,9] The absorption due to oxidation has not been acknowledged.

Figure 2 shows typical Raman spectrum for the present wide-optical-band-gap material (corresponding to the third plot from the left in Fig. 1). It is surprising that the spectrum shows a sharp peak at 514 cm^{-1}, and does not contain $\sim$480 cm^{-1} component, indicating that the silicon atoms in the material are mostly crystallized. The presence of polysilane $(\mathrm{SiH}_2)_n$ crystals is denied, because they show a broad Raman peak near 480 cm^{-1}.[4,10] Moreover, they cause a large shift in the Si—H stretching absorption wave number ($\sim$2120 cm^{-1}) in the infrared absorption spectrum.[4] Concerning the growth mechanism, details are not known at the present stage. However, one of the most probable candidates is the hydrogen plasma-assisted crystallization.[11]

From Figs. 1 and 2, it is suggested that the material consists of small crystalline silicon particles surrounded by hydrogen atoms, which are bonded in the dihydride form. In fact, the material prepared by the present method (both on fused quartz and on single-crystal silicon substrates) revealed polyhedral or spherelike grains in the transmission electron microscope photograph.[12] In order to treat more quantitatively, x-ray diffraction measurements were performed, and the average microcrystal size was deduced from the half-width of the (111) diffraction peak using Scherrer's formula.[13] The center of the diffraction angle $2\theta = 27.9 \pm 0.2°$ [(111) plane for Cu $K\alpha$] shifts towards the low-angle side with respect to that of single-crystal silicon ($2\theta = 28.47°$), indicating that the lattice constant of the microcrystals is about 2% larger than that of the single crystal.[14] This expansion of the microcrystal lattices may be related to the small shift in the Raman peak (514 cm^{-1}) with respect to that of single-crystal silicon (520 cm^{-1}).[15] Figure 3 shows the relationship between optical band gap and the average microcrystal size deduced from x-ray diffraction measurements (open circles). The optical band gap increases with decreasing the microcrystal size, as shown in Fig. 3.

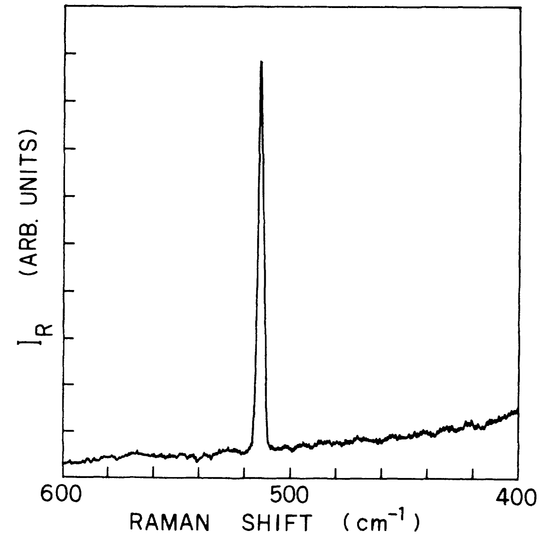

FIG. 2. Raman scattering intensity I_R vs Raman shift for the present wide optical band gap material which corresponds to the third plot from the left in Fig. 1.

In order to confirm the present structure (see inset in Fig. 3) more definitely, the average microcrystal size will be estimated from another method. When the material consists of small spherical silicon particles surrounded by hydrogen atoms (which are bonded in the form of SiH_2), the particle diameter, D, can be estimated from the following equation:[16]

$$D = 6a\frac{1-C_{\mathrm{H}}}{C_{\mathrm{H}}}\ , \tag{1}$$

where a and C_{H} are lattice constant and hydrogen con-

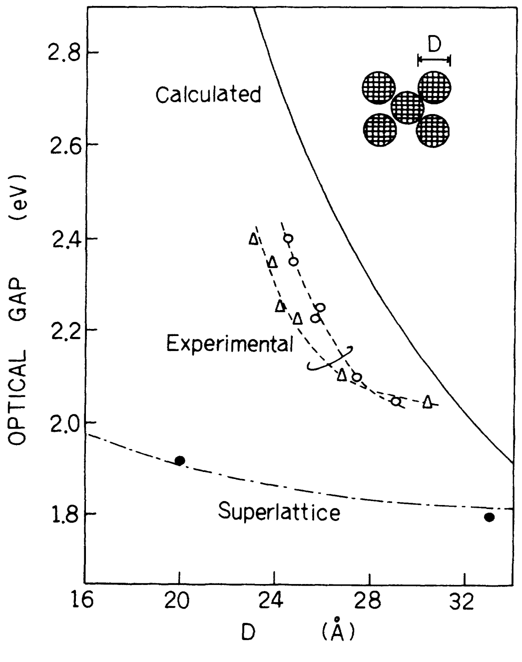

FIG. 3. Optical band gap vs microcrystal size D. D was obtained from both the half-width of the x-ray diffraction peak (open circles) and Eq. (1) (open triangles), as discussed in the text. The solid curve is the energy separation between the highest level in the valence band and lowest level in the conduction band, calculated for the crystalline silicon particles. Solid circles are for a-Si:H/a-SiN$_x$:H superlattices, and the dot-dashed curve is the calculated result for the superlattices (Ref. 5).

tent, respectively. The diameters were deduced from Eq. (1) using the data in Fig. 1, and the results are plotted in Fig. 3 (open triangles). In this calculation, a lattice parameter of $a/a_0 = 1.02$ (a_0: for single-crystal silicon) was used, because the x-ray data showed that the lattice is expanded by about 2% from that of the single-crystal. The plots, thus obtained, fit the experimental curve deduced using the half-width of the x-ray diffraction peak. The result strongly supports the microscopic structure shown in the inset in Fig. 3. Those fine particles may be bound together by van der Waars interaction. There may be also short-chained polysilane [$(\mathrm{SiH}_2)_n$ $n = 1$ or 2 from the infrared absorption data] for interstitial material. However, the former is more plausible, because the presence of a great amount of polysilane is inconsistent with the above discussion concerning the hydrogen content, and with the potential barrier height at the particle surface, as discussed afterward.

The important phenomenon caused by the present microscopic structure is a three-dimensional quantum-well effect. The experimental results shown in Fig. 3, i.e., the increase in the optical band gap with decreasing the particle size, can be explained by the quantum size effect qualitatively. In order to estimate the quantum effect theoretically, a simple model will be applied as follows: Confinement of an electron with effective mass m^* in a three-dimensional spherical well with infinite depth and diameter D increases the ground-state energy of the electron by

$$\Delta = \frac{2\hbar^2\pi^2}{m^* D^2} \; . \tag{2}$$

The solution is a spherical Bessel function, and the eigenvalue Δ increases by a factor of $\frac{4}{3}$ with respect to that of a three-dimensional cubic well with length D. The solid curve in Fig. 3 is the energy separation (the same scale as for the optical band gap) between the highest level in the valence band and the lowest level in the conduction band, calculated on the assumption that the effective masses for both the electrons and holes in the microcrystals are the same as those of single-crystal silicon, and that the band gap of the silicon crystal is 1.1 eV. [Although single-crystal silicon has an indirect gap, this value is used because the experimentally obtained optical band gap deduced from $(\alpha\hbar\omega)^{1/2}$-vs-$\hbar\omega$ plots was 1.1 eV for conventional silicon microcrystals.[7]] The plots marked by a solid circle in Fig. 3 are for the a-Si:H/a-SiN$_x$:H superlattices, in which the band gap of the well material (i.e., a-Si:H) is 1.77 eV. Taking into account the difference in the band gap between the crystal silicon (1.1 eV) and the a-Si:H (1.77 eV), the present materials have a very large optical band gap compared with that predicted by a one-dimensional quantum-well effect. The large shift in the optical band from that of ordinary crystalline silicon can be explained by a three-dimensional one. Note that the conventional silicon microcrystal formation in the binary Si:H materials (a-Si:H has an optical band gap of $1.7 \sim 1.8$ eV) causes a reduction in the optical band gap (< 1.5 eV),[6] whereas the present material has a wide-optical band gap of up to 2.4 eV in spite of the nearly complete crystallization.

The discrepancy in the energy gaps between experiment and theory will be discussed. The theoretical curve in Fig. 3 was obtained assuming a uniform well size, whereas the microcrystal size in the real material should have a deviation, so that the size deduced from Eq. (1) and x-ray diffraction measurements is an average value. In fact, the optical absorption spectrum in the range of 0.2—0.9 μm shows a monotonical change, and does not show many absorption peaks corresponding to the discrete density of states predicted by a uniform three-dimensional quantum well. As shown in the calculated curve in Fig. 3, the change in the size by 2 Å causes the change in the energy separation by about 0.2 eV. Therefore, even a small deviation in the microcrystal size causes a continuous density of states, and also causes a reduction in the energy gap from that predicted by a uniform microcrystal size. There may be also the size effect on the crystal silicon band gap itself. Assuming the presence of a great amount of polysilane for interstitial material, the potential barrier height should be very small ($1 \sim 2$ eV),[3,10] and the obtained wide optical band gap cannot be explained. However, the discrepancy in Fig. 3 may be partly explained by interstitial material formed irregularly between the particles.

In conclusion, we have prepared the materials which consist of small crystalline silicon particles surrounded by hydrogen atoms. They have a large optical band gap of up to 2.4 eV, although they are mostly crystallized. The widening of the optical band gap can be explained by a three-dimensional quantum-well effect in the microcrystals. There are no effects causing a drastic increase in the optical band gap of the mostly crystallized material except for the size effect. The result indicates that the optical band gap of Si:H alloys is very much affected by the microscopic structure as well as the hydrogen content.

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