Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 467-470

S-II-3

Three-Dimensional Quantum Well Effects in Ultra-fine Silicon Particles

Shoji FURUKAWA and Tatsuro MIYASATO

Department of Computer Science and Electronics
Kyushu Institute of Technology
680-4, Kawazu, Iizuka-shi, Fukuoka-ken 820, Japan

We demonstrate the mostly crystallized Si:H having a wide optical band gap and a low electrical conductivity, and showing a visible photoluminescence at room temperature. The materials consist of small crystalline silicon particles (average diameters : 20-50 Å) surrounded by $=SiH_2$ groups. The observed optical and electrical properties are explained by the three-dimensional quantum size effects in the ultra-fine silicon particles.

1. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) was prepared by means of a sputtering,[1] plasma chemical vapor deposition,[2] and other techniques.[3] Microcrystalline Si:H (μc-Si:H) was also prepared by selecting deposition parameters in those methods.[4] The physical properties of the materials were changed with a change in the content of microcrystal, and approached to those of c-Si with increasing the volume fraction of microcrystal.[5] In those previous methods, the content of microcrystal in binary Si:H materials increased with an increase in substrate temperature during the deposition.

In this paper, we report on the binary Si:H materials prepared by means of a new hydrogen plasma sputtering technique with a low substrate temperature of ~100 K. In spite of the low substrate temperature, the obtained materials consist of very small silicon microcrystals, which are surrounded by $=SiH_2$ groups. Surprisingly, the optical and electrical properties are quite different from those of c-Si and conventional μc-Si:H, and they are explained by the three-dimensional quantum size effects in the ultra-fine silicon particles.

2. EXPERIMENTAL

The Si:H 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. The rf power and hydrogen gas (99.99999 % purity) pressure were varied from 20 to 300 W and from 0.2 to 20 Torr, respectively. The material was 0.5-20 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°. In

order to measure the dark- and photoconductivities, aluminum was evaporated onto the surface of the materials on fused quartz substrates. The photoconductivity measurement was performed using a xenon lamp as an excitation light source. The visible photoluminescence was observed at room temperature using an Ar ion laser (5145 Å line) and an optical filter.

3. RESULTS AND DISCUSSION

Typical Raman spectrum for the present material is shown in Fig.1. It shows a sharp peak near 514 cm^{-1}, and does not contain ~480 cm^{-1} component, indicating that the silicon atoms are mostly crystallized. Left inset shows typical infrared absorption spectrum. The appearance of two peaks in the bending mode region (850-900 cm^{-1}) suggests the presence of $(SiH_2)_n$ ($n \geq 1$) or SiH_3 groups.[1,2,6] However, the presence of long-chained polysilane $(SiH_2)_n$ or SiH_3 causes a large shift in the stretching absorption wavenumber (2120-2140 cm^{-1}),[1,2,7] whereas the observed stretching wavenumber is 2090-2100 cm^{-1}. Therefore, it is concluded that the hydrogen atoms are incorporated in the form of $(SiH_2)_n$ (n=1 or 2).[8] From these results, we can construct the microscopic structural model as right inset in Fig.1. It shows the presence of very small silicon microcrystals surrounded by $=SiH_2$ groups. The microcrystal size was deduced from the half-width of the X-ray diffraction peak using Scherrer's formula,[9] and was estimated to be 20-50 Å. In fact, the transmission electron microscope photograph of the material prepared by the present method revealed polyhedral or sphere-like grains ($\lesssim$ 100 Å).[10]

Typical optical absorption spectrum is shown in Fig.2 (dashed curve). It shows a

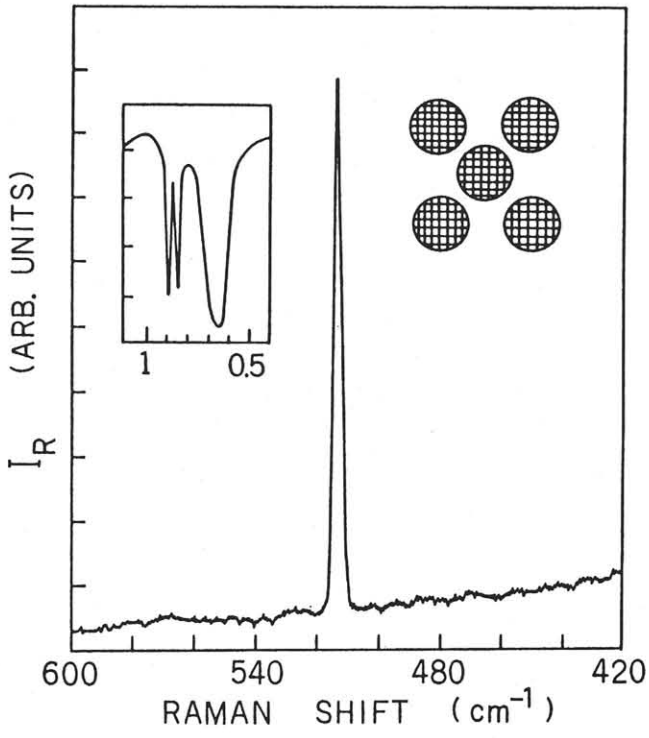

Fig.1 Typical Raman spectrum for the present material (I_R : Raman scattering intensity). Left inset shows typical infrared absorption spectrum (horizontal axis : wavenumber in unit of 10^3 cm^{-1}; vertical axis : transmittance). The ir spectrum indicates the presence of $(SiH_2)_n$ ($n \geq 1$). From the stretching absorption wavenumber (near 2100 cm^{-1}), n was determined to be 1 or 2. From these results and transmission electron microscope and X-ray data, it is concluded that the materials consist of small crystalline silicon particles surrounded by $=SiH_2$ groups (see right inset).

monotonical change, so that the optical gap was deduced from $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ plots, where α and $\hbar\omega$ are absorption coefficient and photon energy, respectively. In spite of the crystallization (see Fig.1), the optical gap is very large (up to 2.4 eV), and is greater by about 1.3 eV than that of conventional μc-Si.[11] The dark-conductivity of the material is also quite different from that of conventional μc-Si and μc-Si:H, and its value is less than 10^{-11} $(\Omega\ cm)^{-1}$ at room temperature. The photoconductivity dependence on incident photon energy shows a blue shift (full curve in Fig.2), and has a peak at $\lambda<0.5$ μm. Surprisingly, the present materials show a visible photoluminescence (red-yellow) at room temperature, although bulk c-Si has an indirect gap. These exciting results observed in the optical and electrical measurements are explained by the quantization of states arising from three-dimensional carrier confinement in the ultra-fine silicon particles.

The energy gap of the material, which consists of ultra-fine silicon particles, has been theoretically estimated.[12] The result can explain the widening of the optical gap. However, the experimentally obtained optical gaps are a little bit smaller than those estimated by the theory. The discrepancy is considered to be caused by the deviation in the microcrystal size in the real material. According to the calculation, the change in the size by 2 Å causes the change in the energy separation by about 0.2 eV.[12] Therefore, even a very small deviation in the microcrystal size causes a reduction in the energy gap from that predicted by a uniform microcrystal size. This also causes a continuous density of states as observed in

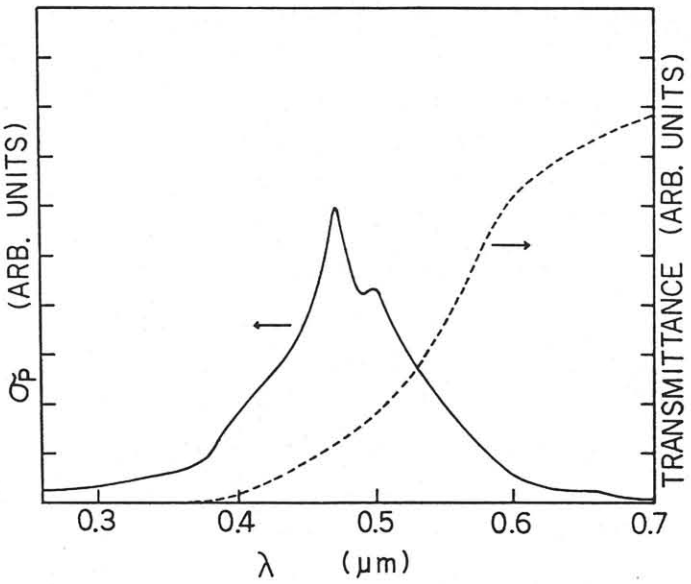

Fig.2 In spite of the crystallization (see Fig.1), optical absorption spectrum (dashed curve) shows a blue shift, and the optical gap determined by $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ (α: absorption coefficient; $\hbar\omega$: photon energy) plots becomes very large (up to 2.4 eV). (Absorption peaks arising from descrete density of states are not observed in this case because of the deviation in the particle size.) Photoconductivity dependence on incident photon energy (full curve) also shows a blue shift (excitation light source : xenon lamp). These materials show a visible photoluminescence (red-yellow) at room temperature (Ar ion laser 5145 Å line excitation).

the optical absorption measurement (see dashed curve in Fig.2). Some of the specimens showed a few broad bands in the optical absorption spectrum, which correspond to the descrete density of states predicted by a uniform three-dimensional quantum well. The details will be published elsewhere.[13)]

4. SUMMARY AND CONCLUSIONS

We have succeeded in fabricating the mostly crystallized Si:H having a wide optical gap of up to 2.4 eV and a low electrical conductivity of less than 10^{-11} $(\Omega\ cm)^{-1}$, and showing a visible photoluminescence at room temperature. These optical and electrical properties are explained by the three-dimensional quantum size effects in the ultra-fine silicon particles.

ACKNOWLEDGEMENT

We thank Professors Shoji Masunaga, Tooru Minami, Masaaki Matsumoto, and Yoshinori Chikaura for their useful advices concerning the measurements. We also thank Professors Susumu Yoshida, Itsujiro Arita, and Torao Yanaru for their encouragement throughout this work.

REFERENCES

1) G.Lucovsky, R.J.Nemanich, and J.C.Knights; Phys.Rev. B 19 (1979) 2064.
2) M.H.Brodsky, M.Cardona, and J.J.Cuomo, Phys.Rev. B 16 (1977) 3556.
3) M.Hirose, M.Taniguchi, and Y.Osaka; Proc. International Conference on Amorphous and Liquid Semiconductors, ed. W.E.Spear, p.352, 1977.
4) A.Matsuda; ibid, ed. K.Tanaka and T.Shimizu, p.767, 1983.
5) T.Hamasaki, H.Kurata, M.Hirose, and Y.Osaka; Appl.Phys.Lett. 37 (1980) 1084.
6) S.Furukawa, M.Seki, and S.Maeyama; Phys.Rev.Lett. 57 (1986) 2029.
7) S.Furukawa, N.Matsumoto, T.Toriyama, and N.Yabumoto; J.Appl.Phys. 58 (1985) 4658.
8) S.Furukawa and N.Matsumoto; Phys.Rev. B 31 (1985) 2114.
9) H.P.Klug and L.E.Alexander; "X-ray Diffraction Procedures" (New York : Wiley-Intersciences) 1981.
10) T.Miyasato, Y.Abe, M.Tokumura, T.Imura, and A.Hiraki; Jpn.J.Appl.Phys. 22 (1983) L580.
11) H.Richter and L.Ley; J.Appl.Phys. 52 (1981) 7281.
12) S.Furukawa and T.Miyasato; to be published in Phys.Rev. B.
13) S.Furukawa, M.Komori, and T.Miyasato; Proc. 19th International Conference on the Physics of Semiconductors, 1988.