

Dependence of microcrystal size on hydrogen gas pressure in silicon-based alloys prepared by reactive laser ablation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 7539

(<http://iopscience.iop.org/0953-8984/3/39/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.147

The article was downloaded on 11/05/2010 at 12:35

Please note that [terms and conditions apply](#).

Dependence of microcrystal size on hydrogen gas pressure in silicon-based alloys prepared by reactive laser ablation

Hiroyuki Fujishiro and Shoji Furukawa

Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology, 680-4 Kawazu, Iizuka-shi, Fukuoka-ken 820, Japan

Received 10 April 1991

Abstract. The silicon-based alloys have been fabricated by means of an excimer laser (XeCl; 308 nm) ablation in a pure hydrogen atmosphere for the first time, and their crystallographic structure has been investigated by an x-ray diffraction method, as a function of hydrogen gas pressure P_{H_2} (0.1–3.0 Torr) during the deposition. As a result, it is found that the alloys prepared at both about 100 and 300 K contain silicon microcrystals, and their size becomes a minimum at $P_{H_2} = 0.5$ Torr. On the other hand, the lattice constant increases monotonically with increasing hydrogen gas pressure in the range of 0.1 Torr $\leq P_{H_2} \leq 3.0$ Torr. The results are discussed in relation to the growth mechanism.

Silicon-based alloys have been used for various devices, such as solar cells [1], thin-film transistors [2] and imaging sensors [3]. Among those alloys, hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) has a relatively large carrier mobility, and its optical properties are also expected to be controlled by changing the size and the distribution of the microcrystals. It has been reported that such microcrystalline materials can be fabricated by reactive sputtering in an Ar–H₂ gas mixture [4], by chemical vapour deposition (CVD) [5–7] and by glow discharge of SiH₄ diluted with Ar and H₂ gas [8]. In these methods the size and the content of microcrystals can be controlled by changing the substrate temperature, the gas dilution ratio and the input electric power during the deposition.

In recent years, a laser ablation method and a laser CVD method have been used for preparing semiconductor and superconductor thin films [9, 10]. Hanabusa *et al* [11] tried to fabricate amorphous silicon (a-Si) films by the laser ablation method. They used a Nd:YAG laser in order to generate the pulsed atomic silicon beams. The vaporization was mainly induced by a 530 nm radiation (the fundamental wavelength was 1060 nm), because a high absorption coefficient could be obtained. Furthermore, they tried to introduce hydrogen gas during the growth and fabricated hydrogenated amorphous silicon (a-Si:H) films using the same instrument [12]. In the case of their experiment, the substrate temperature was kept constant at about 300 K. It has also been reported that a single-crystal silicon film could be obtained at about 970 K by KrF excimer laser ablation [13].

In this paper, the silicon-based alloys have been fabricated onto a low-temperature substrate by means of an excimer laser (XeCl; 308 nm) ablation in a pure hydrogen atmosphere for the first time. The crystallographic structure of the materials obtained

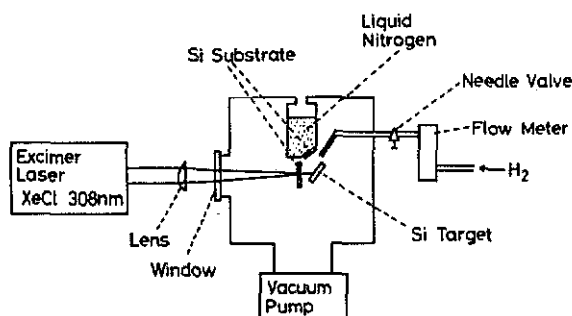


Figure 1. Schematic diagram of the present growth system for excimer laser ablation.

are examined by an x-ray diffraction method. As a result, it is found that the alloys prepared at both about 100 and 300 K contain silicon microcrystals, and their size becomes a minimum at a hydrogen gas pressure P_{H_2} of nearly 0.5 Torr. It is also found that the lattice constant increases monotonically with increasing hydrogen gas pressure in the range of $0.1 \text{ Torr} \leq P_{\text{H}_2} \leq 3.0 \text{ Torr}$. These experimental results are discussed in relation to the growth mechanism.

Figure 1 shows the schematic diagram of the present growth system. An XeCl excimer laser (308 nm) was used for an ablation with a repetition rate of 60 Hz and a duration of 26 ns. The laser beam was focused onto an area of $1 \text{ mm} \times 3 \text{ mm}$ of the target surface in the vacuum chamber through a fused silica window. The fluence of the laser beam was approximately $7\text{--}10 \text{ J cm}^{-2}$. The target was a $10 \text{ mm} \times 20 \text{ mm} \times 2 \text{ mm}$ non-doped single-crystal silicon plate. In order to obtain a constant-ablation condition, the beam position on the target surface was continuously changed. A non-doped single-crystal Si(100) wafer was used as a substrate. The deposition was performed at two substrate temperatures. One was about 100 K, and the other was 300 K. In the former case, the substrates were cooled using liquid nitrogen. The distance between the substrate and the target was about 1.5 cm. After the evacuation, the pure hydrogen gas (99.999 99%) was introduced through a stainless steel nozzle towards the target. The deposition was carried out at a hydrogen gas pressure of $0.1 \text{ Torr} \leq P_{\text{H}_2} \leq 3.0 \text{ Torr}$, which corresponded to a hydrogen gas flow rate of 5–150 sccm. After the laser deposition, the films prepared at about 100 K were heated to room temperature at $P_{\text{H}_2} = 30 \text{ Torr}$. The materials obtained were examined by an x-ray diffraction method. The diffraction from the single-crystal Si(100) substrate does not occur in the present range of diffraction angles.

Figures 2(a) and 2(b) show the Si(111) Bragg reflections from the films prepared at substrate temperatures of about 100 K and 300 K, respectively. The Si(220) and Si(311) Bragg reflections were also observed for all the obtained films. From figures 2(a) and 2(b), it is clear that the crystalline materials are obtained at a very low substrate temperature of about 100 K. It is also clear that the Si(111) diffraction peak slightly shifts towards small angles with increasing P_{H_2} during the deposition. This indicates that the lattice constant of the silicon-based alloys increases on increase in P_{H_2} . It should be noted, however, that the diffraction angle, i.e. the lattice constant, is hardly changed by the change in the substrate temperature (about 100–300 K) during the deposition (see both figure 2(a) and figure 2(b)).

Figure 3 shows the relation between P_{H_2} and the lattice constant of the deposited alloys. The lattice constant was deduced from the Si(111) diffraction peak. From figure 3, it is found that the lattice constant increases on increase in P_{H_2} .

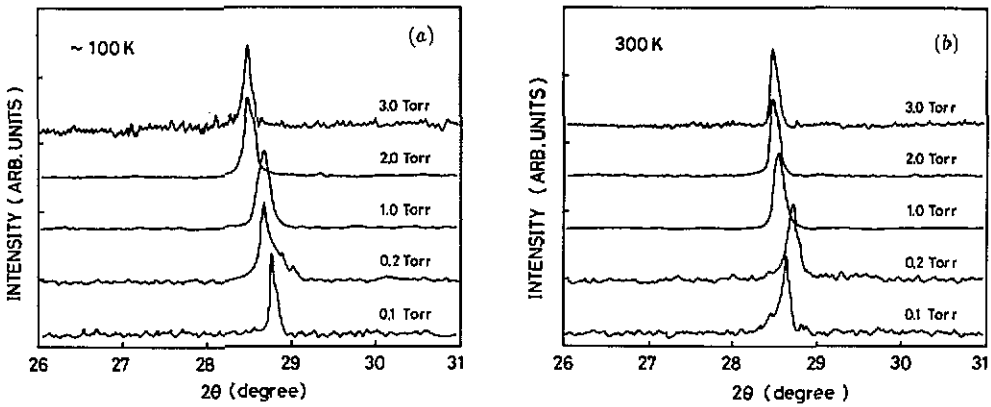


Figure 2. X-ray diffraction patterns (2θ versus scattered x-ray intensity, where θ is the diffraction angle) for the alloys prepared at hydrogen gas pressures of 0.1–3.0 Torr. The substrate temperatures are (a) about 100 K and (b) 300 K, respectively.

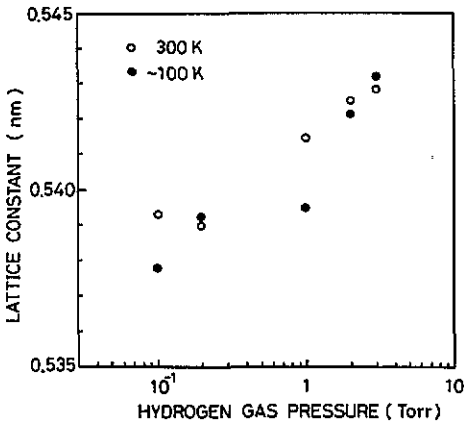


Figure 3. Relation between the hydrogen gas pressure and the lattice constant of the alloys deposited at substrate temperatures of both about 100 K (●) and 300 K (○).

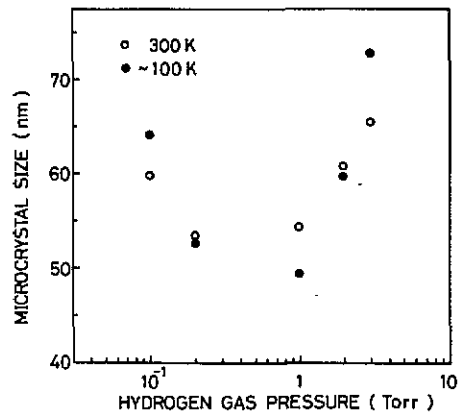


Figure 4. Relation between the hydrogen gas pressure and the size of the microcrystals for the alloys prepared at substrate temperatures of both about 100 K (●) and 300 K (○).

Figure 4 shows the relation between P_{H_2} and the size of the microcrystals. The size was calculated from the full width at half-maximum (FWHM) of the Si(111) reflections in figures 2(a) and 2(b) using Scherrer's formula [14]. It is observed that the size becomes a minimum at $P_{H_2} \approx 0.5$ Torr. The microcrystal size is about 50 nm at $P_{H_2} \approx 0.5$ Torr and is smaller by about 20% than that at 0.1 Torr.

From figures 3 and 4, it is suggested that the effect of the hydrogen gas on the material growth changes at $P_{H_2} \approx 0.5$ Torr. In the range of $P_{H_2} < 0.5$ Torr, the lattice constant and the microcrystal size become increased and decreased, respectively, on increase in P_{H_2} . Silicon atoms and/or clusters are ablated from the target with a high kinetic energy by both a multi-photon and a thermal excitation effect. The fluence of the laser beam is kept constant in this study, so that the number of ablated silicon species is considered to

be constant and do not depend on P_{H_2} . The hydrogen gas around the target surface is also excited to high-energy states, such as hydrogen radicals, by the laser irradiation. Therefore, it is expected that such hydrogen radicals activate the silicon atoms and/or clusters ablated from the target. When P_{H_2} is low, a small amount of excited hydrogen species exists, so that the ablated silicon atoms and/or clusters do not react very much with the hydrogen species. The number of hydrogen species reacting with silicon species is considered to be increased on increase in P_{H_2} . The increase in the lattice constant at $P_{\text{H}_2} < 0.5$ Torr is, therefore, explained by the increase in the hydrogen content in the deposited films. In fact, the infrared absorption measurements showed that the hydrogen content (up to 2 at.%) in the films was almost proportional to P_{H_2} (in the range $0.1 \text{ Torr} \leq P_{\text{H}_2} \leq 0.5 \text{ Torr}$). From figure 4, it is acknowledged that the microcrystal size negatively correlates with the lattice constant in the range of $P_{\text{H}_2} < 0.5$ Torr. Concerning this result, it has been reported that the microcrystal size decreases with increasing hydrogen content in the silicon-based alloys [15], so that the result in figure 4 (in the range of $0.1 \text{ Torr} \leq P_{\text{H}_2} \leq 0.5 \text{ Torr}$) is also explained by the increase in the hydrogen content.

On the other hand, the effects of hydrogen gas on the crystallographic structure changes in the range $P_{\text{H}_2} > 0.5$ Torr. In the present experiment, the size of the plume in front of the target became small in the case of high P_{H_2} , and the emission intensity of the plume became strong on increase in P_{H_2} . It is, therefore, considered that the ablated silicon species collide with hydrogen gas in the vicinity of the target surface for high P_{H_2} , because of the shortening of the mean free path. In such a case, the hydrogen content of the deposited films may be almost saturated. From figure 4, the microcrystal size increases on increase in P_{H_2} for $P_{\text{H}_2} > 0.5$ Torr. Similar results have been reported on the previous work concerning the gas evaporation method [16]. In that method, the microcrystal size increased with increasing ambient inert gas (i.e. Ar or He) pressure. Such a phenomenon has been explained by the reduction in the kinetic energy of the evaporated species due to the collision with the inert gas. The present result is also explained by a similar effect of the hydrogen gas. In our case, the microcrystals are formed by the silicon species, whose kinetic energy is reduced by collision with the hydrogen species. This may cause the increase in the lattice constant for $P_{\text{H}_2} > 0.5$ Torr, as shown in figure 3.

In conclusion, we have fabricated the silicon-based alloys by means of an excimer laser (XeCl; 308 nm) ablation in a pure hydrogen atmosphere for the first time, and their crystallographic structure has been investigated by an x-ray diffraction method, as a function of P_{H_2} during the deposition. Significant results obtained in this paper are as follows.

- (1) The silicon-based alloys, which contain silicon microcrystals, have been obtained at substrate temperatures of both about 100 K and 300 K.
- (2) The microcrystal size of the alloys becomes a minimum at $P_{\text{H}_2} = 0.5$ Torr, whereas the lattice constant increases monotonically with increasing P_{H_2} .

The present method has the advantage of fabrication of microcrystals at a low substrate temperature and is expected to be used for preparing various crystalline materials.

Acknowledgment

We are grateful to Professor Yoshitake Yamazaki for valuable discussions.

References

- [1] Carson D E and Wronski C R 1976 *Appl. Phys. Lett.* **28** 671-3
- [2] LeComber P G 1979 *Electron. Lett.* **15** 181-3
- [3] Yamamoto H 1981 *Japan. J. Appl. Phys. Suppl.* **1** 20 305-9
- [4] Lucovsky G, Nemanich R J and Nights J C 1979 *Phys. Rev. B* **31** 2064-9
- [5] Furukawa S and Matsumoto N 1983 *Phys. Rev. B* **27** 4955-60
- [6] Furukawa S, Matsumoto N, Toriyama T and Yabumoto N 1985 *J. Appl. Phys.* **58** 4658-61
- [7] Furukawa S and Matsumoto N 1985 *Phys. Rev. B* **31** 2114-20
- [8] Spear W E and LeComber P G 1975 *Solid State Commun.* **17** 1193-6
- [9] Mishima Y, Hirose M and Osaka Y 1984 *J. Appl. Phys.* **56** 2803-7
- [10] Inam A, Hedge M S, Wu X D, Venkatesan T, England P, Miceli P F, Chase E W, Cheng C C, Tarascon J M and Watchman J B 1988 *Appl. Phys. Lett.* **53** 908-11
- [11] Hanabusa M, Suzuki M and Nishigaki S 1981 *Appl. Phys. Lett.* **38** 385-7
- [12] Hanabusa M and Suzuki M 1981 *Appl. Phys. Lett.* **39** 431-3
- [13] Lubben D, Barnett S A, Suzuki K, Gorbalkin S and Greene J E 1985 *J. Vac. Sci. Technol. B* **3** 1081-6
- [14] Klug H P and Alexander L E 1974 *X-ray Diffraction Procedures* (New York: Wiley)
- [15] Fujishiro H and Furukawa S 1990 *Solid State Commun.* **73** 835-8
- [16] Granqvist C G and Buhrman R A 1976 *J. Appl. Phys.* **47** 2200-7