

Crystallization Mechanism of Nanocrystalline Silicon Fabricated by Hydrogen Radical Annealing

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We have investigated the crystallization mechanism of nanocrystalline silicon (nc-Si) fabricated by alternating deposition of hydrogenated amorphous Si (a-Si:H) and hydrogen radical annealing. By using this method, we can control the nucleation and growth process of nc-Si independently. Nucleation takes place on the a-Si:H surface sufficiently passivated by hydrogen. Growth of nc-Si is caused by hydrogen radicals diffused through a-Si:H to the nuclei.

§1. Introduction

A fine structure of silicon (Si) with the size of less than 10nm is expected to exhibit quantum size effect and can be an essential for next-generation Si ultra large scale integrated circuit (ULSI). However, one big problem is a lack of the technology to fabricate such a fine structure. Nanocrystalline Si (nc-Si) has a potential to solve this problem.

Nanocrystalline silicon (nc-Si) is consisted of ultrafine particle of Si with grain size of less than 10 nm. Thin films of nc-Si have conventionally been prepared by plasma enhanced chemical vapor deposition (PECVD) with SiH₄ highly diluted by H₂. However, this method cannot control grain size and grain site of nc-Si, precisely. Then, in order to simplify the growth mechanism of nc-Si and to provide a new degree of freedom in growth technology of nc-Si, we separate deposition and crystallization of Si film by using the method alternating deposition of hydrogenated amorphous Si (a-Si:H) and hydrogen radical annealing.¹⁾ In our recent study, it is suggested that the growth of nc-Si is caused by the diffusion of hydrogen radicals into a-Si:H layer.²⁾ In this paper, we discuss crystallization mechanism of nc-Si fabricated by this method.

§2. Experimental

To fabricate nc-Si, a capacitively coupled plasma enhanced chemical vapor deposition (PECVD) system was used. The high frequency electric power of

144MHz in very high frequency (VHF) band, was supplied to the power electrodes which are 6cm in diameter with 3.4cm apart.¹⁾ At the step of the deposition of a-Si:H, a gaseous mixture of SiH₄ and H₂ was fed into the reaction chamber. In the step of hydrogen radical annealing, only H₂ was fed by interrupting the supply of SiH₄. Hydrogen radicals generated in the H₂ plasma reached on the surface of a-Si:H films.

Deposition parameters were set as follows: the substrate temperature was 250°C. The flow rate of SiH₄ and H₂ was 12sccm and 54sccm, respectively (i.e., SiH₄:H₂ = 2:9). For the deposition of device grade a-Si:H, the VHF power was 2W (i.e., the power density was 71mW/cm²) and the pressure was 0.14Torr. In the stage of hydrogen radical treatment, the VHF power was 3W (i.e., 110mW/cm²) and the pressure was 0.1Torr. By exposing to H₂ plasma of this condition, a-Si:H is etched with a rate of about 0.01nm/s. Rise and fall time of the pulsed supply of SiH₄, defined as the time to reach 90% of the saturated value, deduced from optical emission spectroscopy, are less than 1s. These time constants are negligible compared to the time employed in the following experiments. Films were deposited on wet oxidized Si(100).

§3. Results and Discussion

In order to clarify the crystallization mechanism, we investigated a series of experiment with two

different time sequences of the plasma processing as mentioned below sequence-[A] and -[B]. Deposited films were characterized by plane transmission electron microscopy (TEM) and transmission electron diffraction (TED).

The schematic diagrams of sequence-[A] and -[B] are shown in Fig.1 (a) and (b), respectively. The sequence-[A] is as follows: First, a-Si:H was deposited on SiO₂ for 100s (the thickness of ~30nm). Then the film was annealed by hydrogen radicals for 40s, followed by the second deposition of a-Si:H for 20s (~7nm). In the sequence-[B] in Fig.1 (b), hydrogen radical annealing of very short time (5s) was inserted after the first deposition of a-Si:H for 90s in the sequence-[B].

Figure 2(a) and (b) show plane TEM images of the films prepared by the sequence-[A] and -[B], respectively. Insets of Fig. 2(a) and (b) are TED patterns. Both featureless TEM image and halo of TED pattern in Fig. 2(a) prove that the structure of the film fabricated by sequence-[A] is amorphous. Both TEM image containing dark spots and ring pattern of TED suggest that the structure of the film produced by the sequence-[B] is nanocrystalline.

The difference between the sequence-[A] and -[B] is only whether or not a layer treated by hydrogen radicals is embedded inside first a-Si:H layer. These results are summarized as follows:

<1> From the result of Fig. 2(a), the structure of the film deposited after hydrogen radical annealing, is still amorphous.

<2> Because the structure of the film after hydrogen radical annealing is influenced by the layer several nm below from the surface, growth of nc-Si is

caused by the diffusion of hydrogen radicals.

<3> Nuclei for nanocrystallization are formed by hydrogen radical annealing, i.e., in these experiments 5s hydrogen radical annealing explained in Fig. 1(b).

Matsuda^{3,4)} proposed a model in which excess H atoms realize adequate hydrogen coverage of the growing surface which enhance the radical diffusion on the surface, resulted in formation of microcrystalline Si (μ c-Si). The mechanism of nucleation, described in result <3>, can be explained by using this "hydrogen coverage model" by Matsuda. At the beginning of a-Si:H deposition, the surface of a-Si:H is sufficiently passivated by hydrogen, caused by hydrogen radical annealing. Then, the surface is the condition for the growth of μ c-Si. However, after the deposition of some atomic layer of Si, the atmosphere of the growing surface changes to the condition for the growth of a-Si:H, i. e., the passivation of a-Si:H surface is not enough for hydrogen radicals to diffuse resulted in nanocrystallization. Then, very small nc-Si particles consisted of several atoms, i. e., nuclei, are formed at the interface between first and second a-Si:H layer.

§4. Conclusions

It has been separated the nucleation process and crystallization process in the fabrication of nc-Si, using alternating deposition of a-Si:H and hydrogen radical annealing. The mechanism of the nucleation to nanocrystallize can be explained by hydrogen coverage model. Growth of nc-Si is caused by hydrogen radicals diffuse through a-Si:H to the nuclei. Now, we will be able to control both the nucleation and the growth of nc-Si, independently.

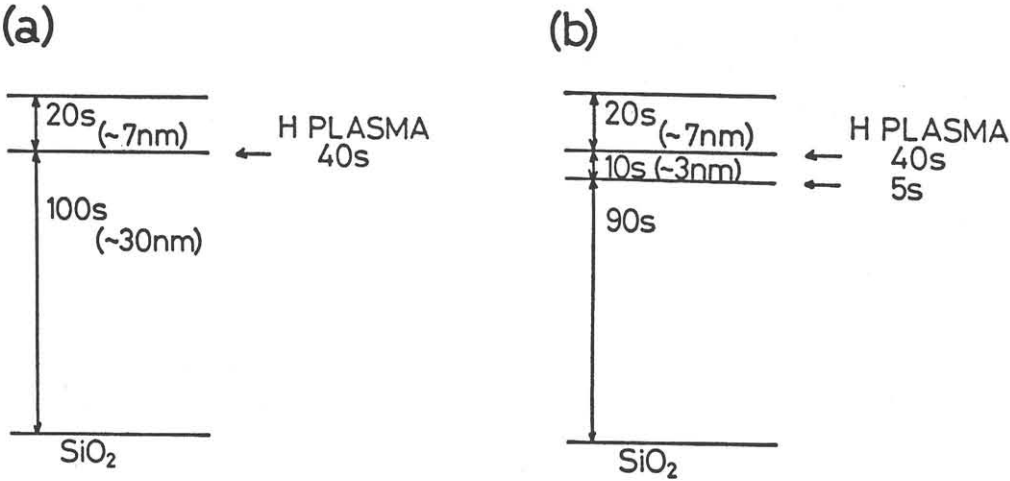


Fig.1: Schematic diagram of experiments. Figure (a) and (b) are diagrams of the sequence-[A] and -[B], respectively.

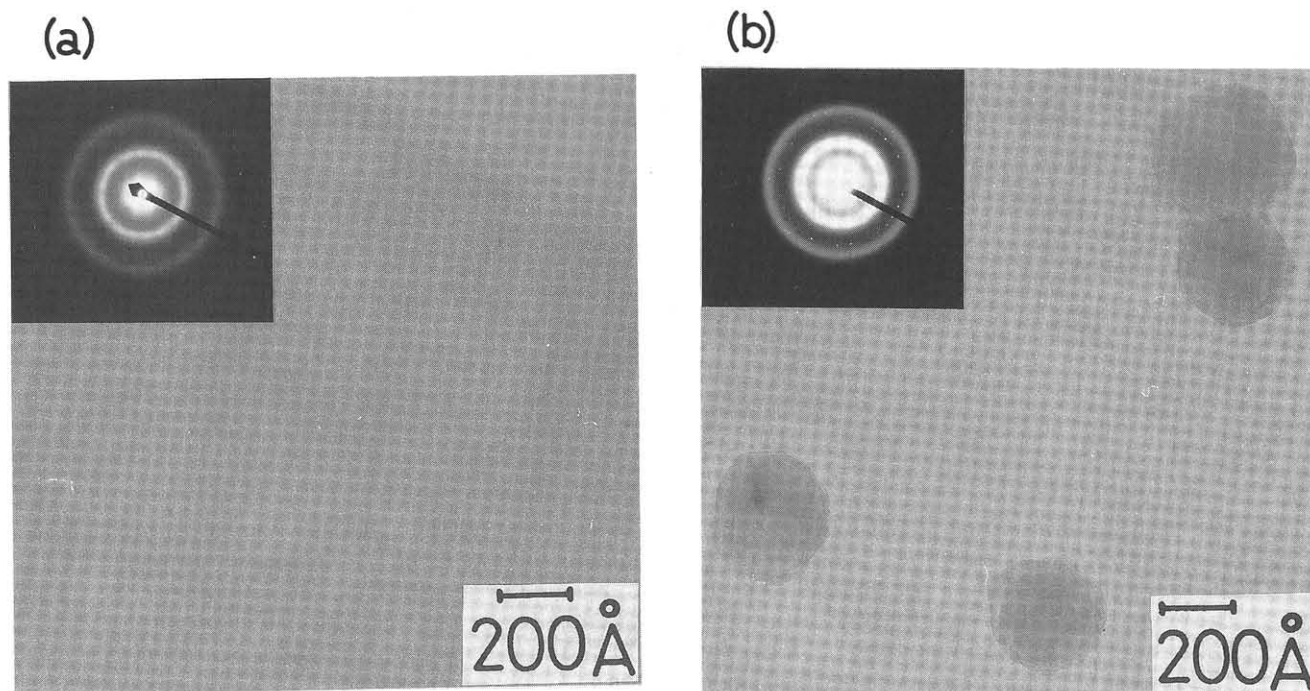


Fig.2: Plane TEM images of the films prepared by alternating deposition of a-Si:H and hydrogen radical annealing. Figure (a) and (b) are images fabricated by the sequence-[A] and -[B], respectively. Insets are TED patterns. The structures of the film formed by sequence-[A] and [B] are amorphous and nanocrystalline, respectively.

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