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Crystallized Si layer properties of novel aluminum-induced crystallization

Doo Won Lee, Muhammad Fahad Bhopal, Soo Hong Lee *

Green Strategic Energy Research Institute, Department of Electronics Engineering, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul, Korea

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ABSTRACT

Aluminum-induced crystallization (AIC) is usually used for making silicon seed layer. In this paper, we investigated the AIC process varied with different diffusion barrier materials. The barrier materials were native Al oxide, directly deposited Al_2O_3, and SiO_2 in AIC process. The effects of these diffusion barrier materials were analyzed by using electron backscatter diffraction (EBSD), Raman spectroscopy, field emission scanning electron microscope (FE-SEM). The results showed that the case of native Al oxide showed diffusion-limited aggregation which usually resulted in polycrystalline structure. On the other hand, the case of SiO_2 layer showed kinetic-limited aggregation, which generally resulted in the mono-crystalline structure. Therefore, we introduced the novel AIC process with SiO_2 layers.

1. Introduction

The aluminum-induced crystallization (AIC) process is one of the methods for enlarging Si grain sizes of thin-film polycrystalline (TFPC) Si solar cells. The conventional AIC process is as followed. First, Al is deposited on foreign substrates such as graphite [1], alumina [2], glass [3], etc. Then, native Al oxide layer is grown by exposure to air. After that, the Si layer is deposited on native Al oxide. Al/native Al oxide/Si structure is annealed below the eutectic temperature (577 °C) of Al and Si for crystallization of Si. The Al and Si layer is exchanged after the annealing process, which is called the Al induced layer exchange (ALILE) process [3]. In the conventional AIC process, the native Al oxide layer is important since the layer is used as one of the Si diffusion paths. Therefore, research trends are usually related with native Al oxide layer, such as increasing thickness of native Al oxide for enlarging Si grain size [4, 5].

Especially, novel AIC using SiO_2 layer instead of native Al oxide layer was newly tried as a seed layer formation method in this paper. Properties of crystallized Si were compared with the conventional and novel AIC process. Moreover, 2 nm of Al_2O_3 was deposited as a reference.

2. Experiment

Graphite substrate (Mersen, Korea) was used as a foreign substrate. The $SiO_x/SiN_x/SiO_x$ layers were deposited using plasma enhanced chemical vapor deposition and flowable oxide methods in order to prevent diffusion of impurities from graphite substrate and planation. The Al and Si layer were deposited using a thermal and electron-beam evaporator in 2.0 10^{-6} Torr, and the deposition rate was controlled between 1.0 and 1.5 Å/s using thickness monitor (STM-100/MF). Then each layer has 400 nm thickness. Before Si deposition, the SiO_2 was deposited without exposure to air between Al and Si layers. The deposition rate was 0.1 Å/s. 2 nm of Al_2O_3 was also separately deposited with the same deposition rate as a reference. Moreover, another sample was exposed to air for 24 h as another reference sample, referred to as conventional AIC reference. After oxide layer and Si deposition, these samples were annealed for 40 h to perfect Si crystallization.

3. Results and discussion

Firstly, Raman spectroscopy was used to analyze quality of crystallized Si which was made by novel AIC, conventional AIC, and 2 nm Al_2O_3 deposited AIC. The result of Raman spectroscopy showed the intensity as a function of Raman shift (Fig. 1). Normally, the a-Si had an intensity of 480 cm^{-1} Raman shift, and the c-Si had an intensity of 520 cm^{-1} Raman shift. High crystallinity Si layer showed smaller full width at height maximum (FWHM) of the Raman spectroscopy at 520 cm^{-1} Raman shift [6]. As a result of Raman spectroscopy, the conventional AIC and novel AIC had high quality crystalline Si properties since both samples had a Raman shift peak at 520 cm^{-1}. On the other hand, the novel AIC had higher quality Si due to the novel AIC had narrow the FWHM than the conventional AIC.

The surface morphology was analyzed by a field emission-scanning electron microscope (FE-SEM) (Fig. 2). In the case of

* Corresponding author.
E-mail address: shl@sejong.ac.kr (S.H. Lee).

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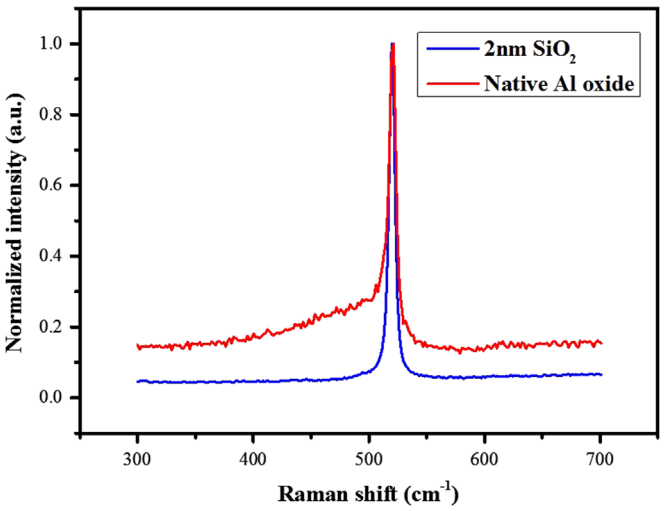

Fig. 1. Raman spectroscopy analysis results of the crystallized Si dependence on the oxide materials.

conventional AIC, the surface morphology showed dendritic structure known as the Brownian tree. The Brownian tree was usually formed by the diffusion-limited aggregation model [7, 8]. The diffusion-limited aggregation model showed that diffusion was a dominant factor for nucleation. Therefore, the diffusion-limited aggregation system determined the surface morphology of the crystalline structure by slow atomic diffusion. This diffusion-limited aggregation was also shown in the Al_2O_3 deposited samples. The Brownian tree was evidently shown when diffusion-limited aggregation phenomenon was strong, such as native Al oxide. The Al_2O_3 samples, which were formed by exposure on air and directly deposited Al_2O_3, thus had slow Si diffusion velocity. On the other hand, in the case of SiO_2 layer, the surface was almost covered with crystallized Si. The reason for this difference between SiO_2 and Al_2O_3 was that the Si nucleation with SiO_2 layer was shown in kinetic-limited aggregation. The kinetic-limited aggregation phenomenon was shown in the system which had enough atom diffusion velocity. Hence, the SiO_2 layer had faster Si diffusion velocity than native Al oxide and 2 nm Al_2O_3 layer. In theory, the crystallized Si layer with diffusion-limited aggregation usually showed polycrystalline structure. However, the case of kinetic-limited aggregation showed single crystalline structure [9]. Therefore, in this paper, the SiO_2 layer was the recommended method for enlarging Si grain size due to the kinetic-limited aggregation had larger crystalline structure than diffusion-limited aggregation in theory.

The crystallized Si was analyzed by electron backscatter diffraction (EBSD) which was a useful technology for measuring Si grain size and plain direction (Fig. 3.). While the novel AIC had expected to enlarge grain size by kinetic-limited aggregation, a trend of Si grain size differed from the results of surface morphology. The average Si grain size of the conventional AIC was larger than the novel AIC. These results were related with the Si nucleation theory in the AIC process. First, the Si nucleation was mainly started in the Al grain boundaries and the Al/a-Si interface (oxide layer) when the Si concentration increased in saturation Si concentration [10]. Second, the Al layer which was deposited by the electron beam evaporator had naturally nano-crystalline structure. The deposited Al grain size grew during the ALILE annealing process. Once nucleated, Si grains in Al grain boundaries had no influence each other [8]. Therefore, these mechanisms effected to the Si nucleation in the AIC process. The AIC processes which used native Al oxide and deposited Al_2O_3 needed more time to reach saturation Si concentration since the Al oxide layers had slower Si diffusion velocity than the SiO_2 layer. Moreover, the deposited Al grain size also grew during the AIC annealing process. In the case of the conventional AIC and 2 nm Al_2O_3 deposited AIC processes, the primary Si nucleation sites in the Al grain boundaries had longer distance than the novel AIC since the Al grain sizes increased during the annealing time to reaching saturation Si concentration. Besides, in the case of the novel AIC, the primary Si nucleation sites in the Al grain boundaries had shorter distance than the conventional and Al_2O_3 deposited AIC. So as the time to reach saturation Si concentration took less, the Al grain sizes had smaller than the conventional and Al_2O_3 deposited AIC. The Al

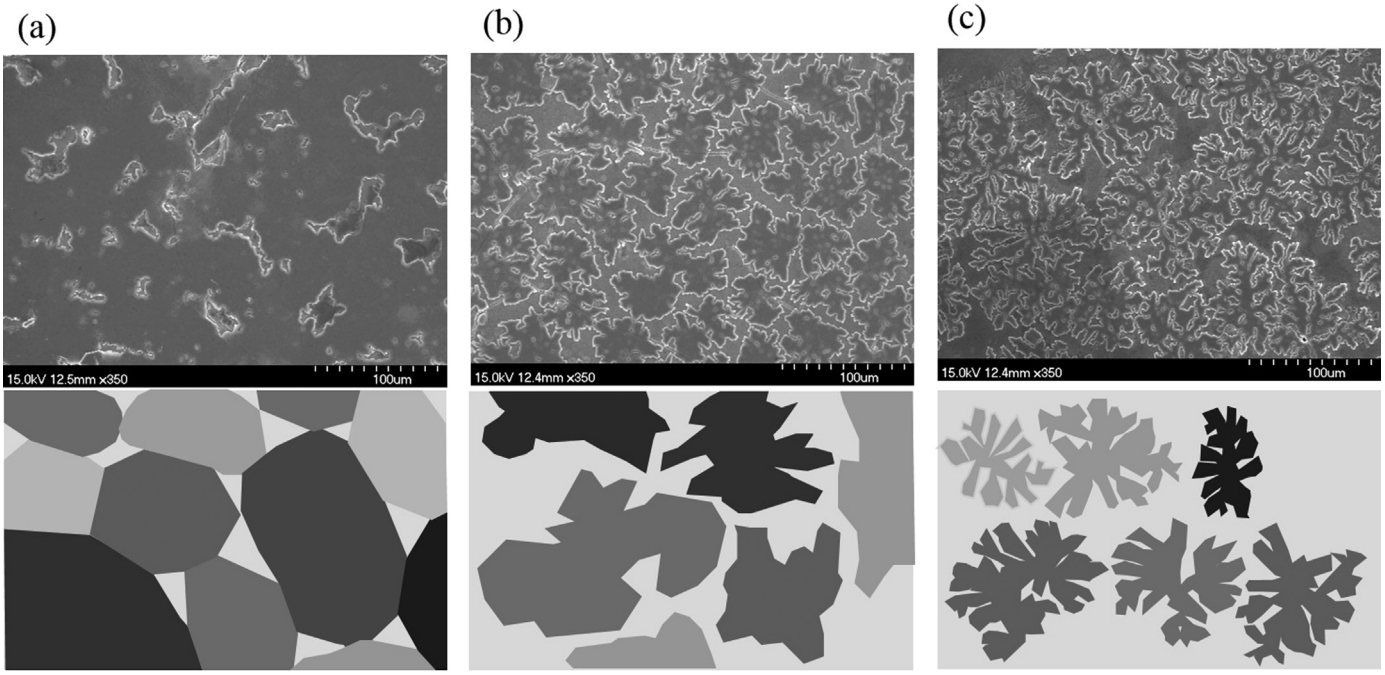

Fig. 2. FE-SEM surface morphology images of crystallized Si which is made by AIC process with (a) SiO_2-2 nm, (b) Al_2O_3-2 nm, and (c) native Al oxide.