Microcrystalline Silicon Film Growth on a Fluoride Film Coated Glass Substrate

Do Young Kim, Joong Hyun Park, Byung Jae Ahn, Jin Su Yoo and Junsin Yi
New material Lab., School of Information and Communication Engineering,
SungKyunKwan University, Kyunggi-do, Suwon, 440-746, Korea
Phone:+82-31-290-7139, E-mail: yi@yurim.skku.ac.kr

Abstract

Various fluoride films on a glass substrate were prepared and characterized in order to determine the best seed layer for a microcrystalline silicon (μc-Si) film growth. Among the various group-IIA-fluoride systems, the CaF_2 *films on glass substrates illustrated (220) preferential orientation and a lattice mismatch of less than 0.7% with Si.* CaF_2 *films exhibited a dielectric constant between 4.1~5.2 and an interface trap density* (D_{it}) *as low as* 1.8×10^{11} $cm^{-2}eV^{-1}$. *Using the* CaF_2*/glass structure, we were able to achieve an improved μc-Si film at a process temperature of 300℃. We have achieved the μc-Si films with a crystalline volume fraction of 65%, a grain size of 700 Å, and an activation energy of 0.49 eV.*

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) films are found in a broad range of electronic devices such as sensors, radiation detectors, photovoltaic (PV) devices, thin film transistors (TFTs), display devices, and memory device applications[1-5]. However, a-Si:H detectors and TFTs show some limitations because of their low carrier mobility. In this study, we focused our research on a seed material that can provide the same surface nature as crystalline silicon (c-Si). Seed materials make it possible to grow μc-Si films at a low substrate temperature by providing the c-Si like surface. Fluoride films such as calcium fluoride (CaF_2), strontium fluoride (SrF_2), and barium fluoride (BaF_2) have the same cubic structure as c-Si as well as the same lattice constant. These characteristics of fluoride films were exploited in device applications of epitaxial silicon on insulators (SOI)[6-7]. Seed layers for μc-Si film growth on fluoride films should meet the following requirements: (1) low lattice mismatch with crystalline Si, (2) low leakage current, (3) high breakdown field, (4) uniform surface, (5) high stability, (6) high reproducibility, and (7) cubic or diamond like crystalline structure. The goal of our research was to determine the best materials and process conditions for a seed layer on a glass plate. We also report the characteristics of the μc-Si film grown on a fluoride coated glass substate..

2. Experiment

The glass substrate, a Corning 1737 glass plate, was cleaned with acetone and methanol, rinsed with DI water, and blow-dried in a nitrogen gas. The CaF_2 thin films were then grown at a base pressure as low as 10^{-6} Torr. The substrate temperature was maintained using four sets of 200W halogen lamps. Pallet-type fluoride sources (3~5 mm) with a purity of 99.95 % were used for the film growth. Prior to μc-Si film growth, we investigated the optimal CaF_2 preparation conditions and conducted the experiment using the best results. The seed layer preparation conditions involved a substrate temperature between 200℃ and 300℃, a fixed growth rate of 0.08 Å, and a film thickness of about 1500 Å. Before the deposition of the μc-Si film, the vacuum pressure for the RPCVD system was maintained below 10^{-7} Torr by using a turbo molecular pump. A diluted silane gas (20% SiH_4 in He gas) was decomposed by using He^+ ions, and the thickness of μc-Si films varied from 500 Å to 2800 Å. The other μc-Si film growth conditions were optimized primarily for the best crystallinity. The prime fixed process parameters were found $[SiH_4]$ = 0.4 sccm, $[H_2]$ = 32 sccm, [He] = 100 sccm, rf power = 50 W, and the total gas pressure (p_{total}) of 98 mTorr. To acquire an accurate substrate temperature, we calibrated the inner thermocouple of heater with other thermocouple on the surface. A multiple point measurement using a Tencor α-step system was employed to minimize the error of the film thickness to below 10%. The crystal volume fraction and the crystal structure of the μc-

Si/CaF_2/glass films were estimated using Raman spectroscopy and X-ray diffraction (XRD), respectively. The films' electrical characteristics were estimated with the dark- and the photo-conductivity ratio (σ_{ph}/σ_d) and the current-voltage-temperature (I-V-T) characteristics. A surface morphology study was performed by using scanning electron microscopy (SEM) and atomic force microscopy (AFM)

3. Result and Discussion

We placed the CaF_2 seed layer on a glass substrate and then deposited the μc-Si films. Prior to the examination of the seed layer effect, RPCVD process conditions were optimized with Si films on a glass substrate. The optimal RPCVD process conditions were given with 50 W RF power, 300°C substrate temperature, 88 mTorr chamber pressure, and 1.2 % SiH_4/H_2 ratio. Using the Raman spectroscopy and an XRD, we evaluated the crystalline structure of thin film Si with and without the CaF_2 seed layer grown at 200°C. Figure 1 illustrates the Raman spectroscopy of μc-Si/CaF_2/glass, a-Si:H/SiO/glass, and c-Si. The Raman shift peak appears at 480 cm^{-1} for an amorphous Si film and 520 cm^{-1} for c-Si. These Raman results can be used to deduce the crystallization volume fraction (X_c) of a thin film Si[8]. The ratio of the crystallized volume fraction is represented by $X_c=I_c/(I_c+\sigma I_a)$, where I_c is c-Si peak intensity and I_a is a-Si:H peak intensity. For a μc-Si film we can take the correction factor as unity ($\sigma \approx 1$). Using the CaF_2 seed layer on glass substrate, we were able achieve the μc-Si film with a crystalline volume fraction of 65%.

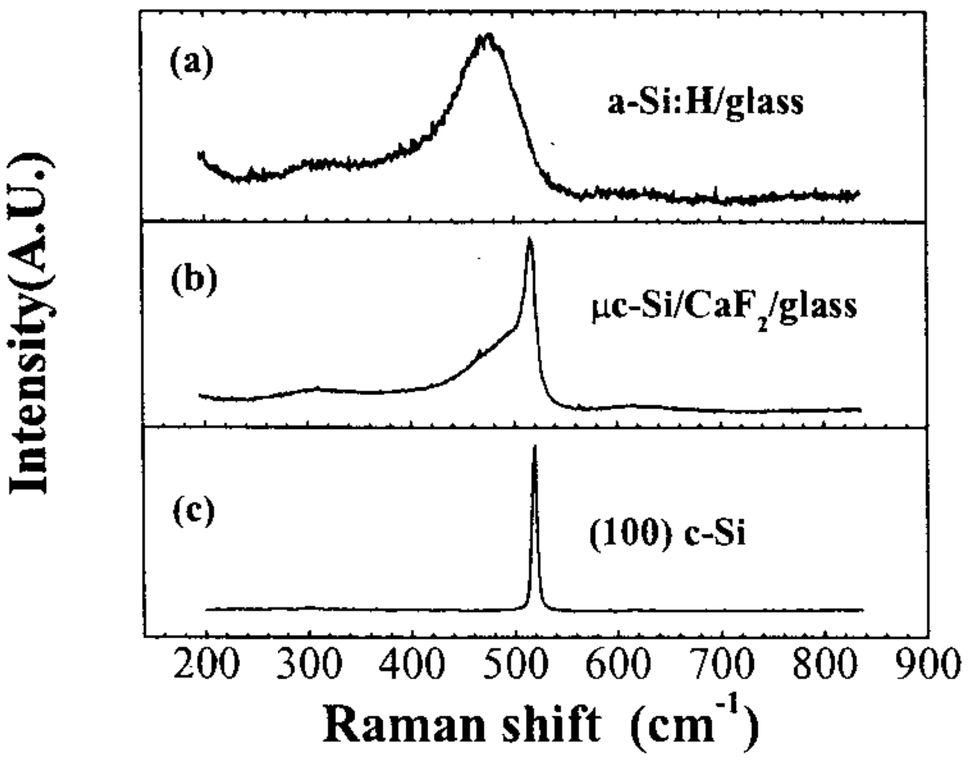

Figure 1. Raman spectroscopy results for (a) a-Si:H/glass, (b) μc-Si/CaF_2/glass, and (c) c-Si.

The μc-Si film crystal orientations were examined by using an XRD method. Figure 2 illustrates the XRD results of thin film Si with and without a seed layer. Thin film Si deposited on the CaF_2 coated glass substrate exhibited a crystalline peak corresponding to (111) and (220) planes.

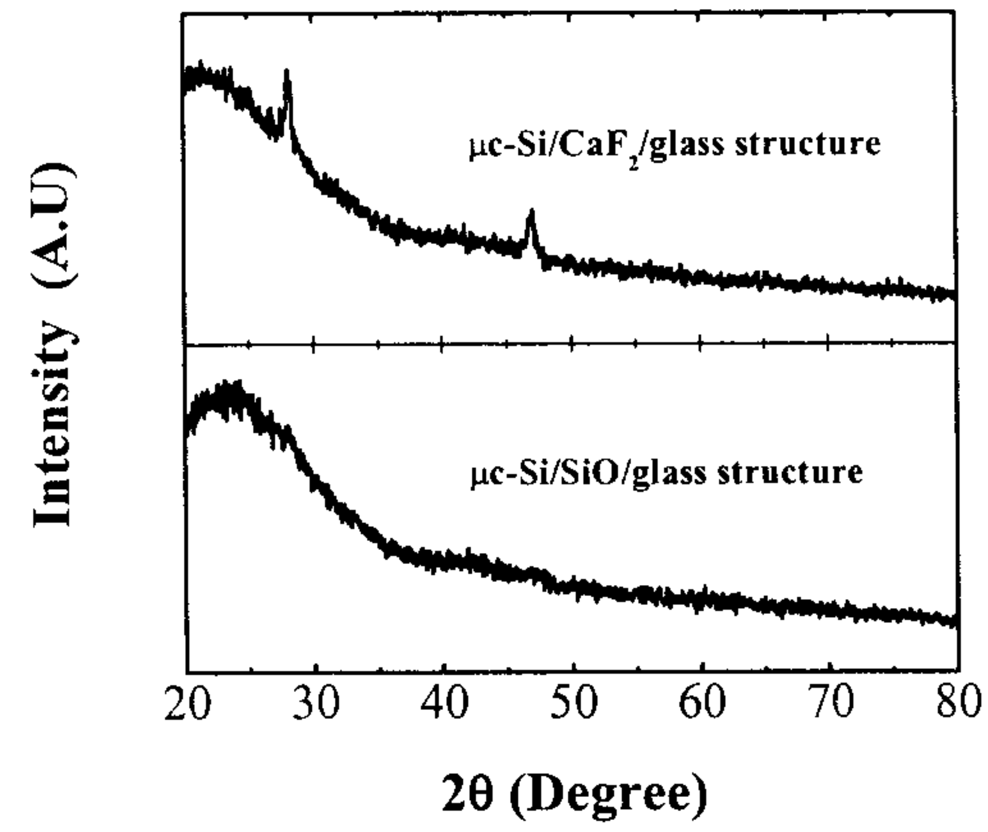

Figure 2. X-ray diffraction patterns on a-Si:H/SiO /glass and μc-Si/CaF_2/glass samples.

The XRD results demonstrate that no crystalline peak for the sample having the SiO layer as shown in Fig. 2. These results suggest that the crystallization of a thin film Si be assisted by the existence of CaF_2 film. The orientation of μc-Si/CaF_2/glass substrate exhibited Si peaks corresponding to (111) and (220) planes. The grain size of the thin film Si was determined by using SEM surface morphology examinations. Figure 3 shows that the average grain size enlarged from 375 Å for a-Si:H/SiO/glass to 700 Å for μc-Si/CaF_2/glass. The SEM results indicate that we can almost double the grain size by replacing the SiO buffer layer with the CaF_2 seed layer.

For electrical property measurement, we have used an inter-digit type grid metal on the surface of the μc-Si/CaF_2/glass and a-Si:H/glass samples. A magnesium metal electrode formed an Ohmic contact with the intrinsic μc-Si films[9]. Activation energy (E_a) measures carrier transition from an intrinsic level to a conduction band. The activation energy can be evaluated from the I-V-T properties of an intrinsic Si using an Arrhenius equation. Figure 4 shows dark conductivity (σ_d) properties as a function of measurement temperature.

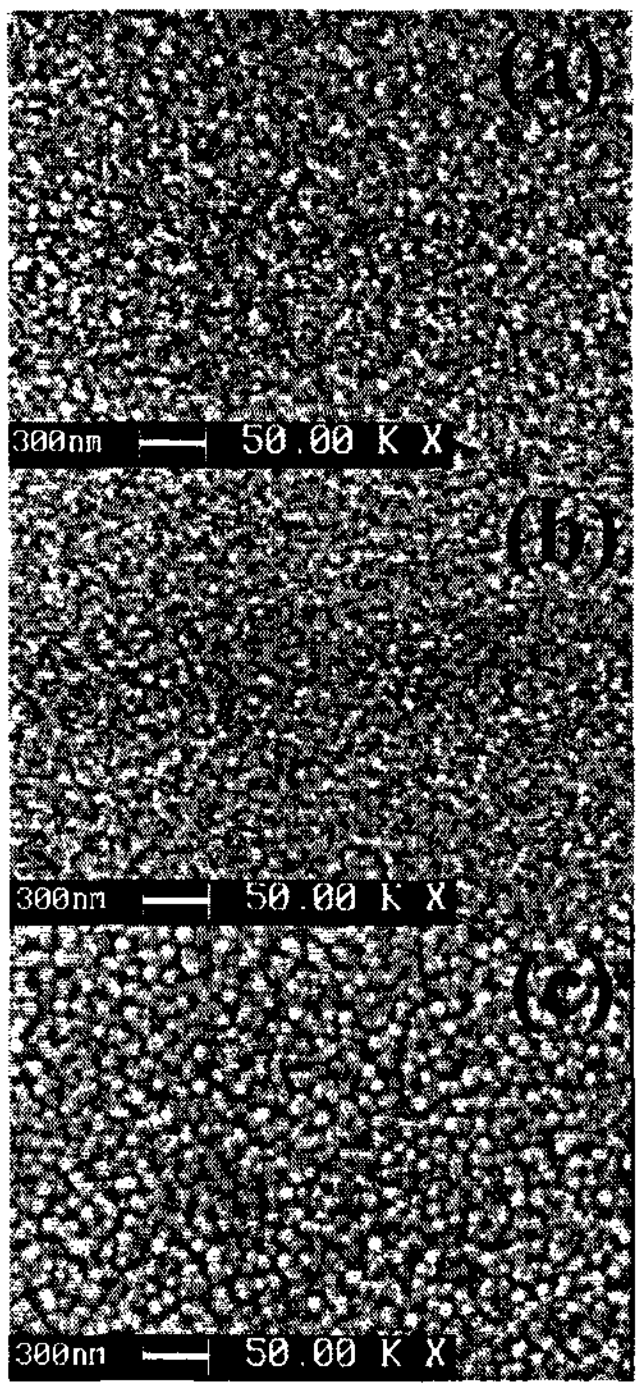

Figure 3. SEM surface image of (a) a-Si/glass, (b) a-Si:H/SiO/glass, and (c) μc-Si/CaF$_2$/glass (Magnifi -cation: x50,000).

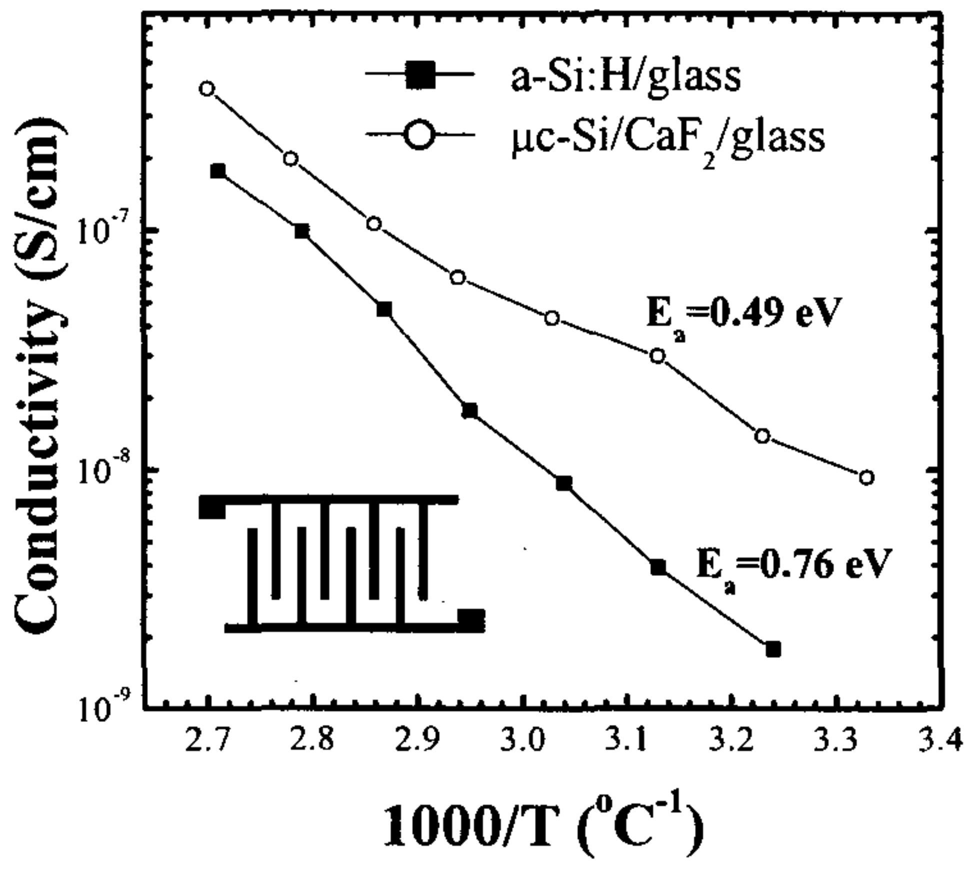

Fig. 4. Conductivity as a function of measurement temperature for μc-Si/CaF$_2$/glass and a-Si:H/SiO /glass sample.

For an intrinsic c-Si, the ideal value of activation energy equals 0.55 eV. Activation energy illustrated 0.49 eV for μc-Si/CaF$_2$/glass and 0.76 eV for a-Si:H/SiO/glass. From the activation energy study, we have noticed that the μc-Si films on a fluoride coated glass substrate are well crystallized. Over the investigated temperatures, dark conductivity changed from 3×10^{-8} S/cm to 4×10^{-7} S/cm for μc-Si/CaF$_2$/glass structure. Photoconductivity (σ_{ph}) was measured under a light intensity of 100 mW/cm^2. Photosensitivity (σ_{ph}/σ_d) showed 1.08x10^4 for Mg/a-Si:H/SiO/glass and 1.24x10^2 for Mg/μc-Si/CaF$_2$/glass structure. This result indicates that we need thicker μc-Si films for thin film Si solar cells. Figure 5 shows the transmittance properties of CaF$_2$ films grown at the various temperatures. From the transmittance spectra, we found that the transmittance of CaF$_2$ films is strongly increased at wavelengths above 300 nm. However, film growth temperature was not a key factor in transmittance variations of CaF$_2$ films. Transmittance of the CaF$_2$ films remained close to 90% for wavelengths between 350 nm and 900 nm. The optical band gap of CaF$_2$ film was calculated to be about 4.5 eV. These results indicate that CaF$_2$ films transmit a wide spectrum of incident light beams for window layer of Si solar cells. The structure of metal/μc-Si/CaF$_2$/glass can be utilized in solar cell application by exposing the glass substrate side to a light source. Because of the excellent transmittance characteristics of CaF$_2$ films, we conclude that μc-Si films deposited on a fluoride coated glass substrate can be applied to improve the efficiency of solar cells.

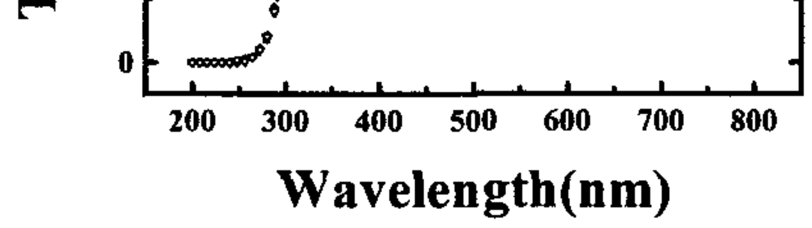

Figure 5. Transmittance versus wavelength for the CaF$_2$ films coated at the various temperatures on a glass substrate.

4. Conclusion

This paper investigated a direct growth of μc-Si film at a low temperature of 300℃ using a CaF$_2$ film layer. From the Raman spectroscopy study, we observed high quality μc-Si film for a deposition pressure of 88 mTorr and highly diluted SiH_4/H_2 gas ratio of 1.2%. Employing a CaF_2 layer, a crystalline volume fraction of μc-Si film was improved to 62 %. XRD results showed μc-Si films are grown in (111) and (220) planes by putting CaF_2 seed layers on glass substrate. Grain size of μc-Si was improved more than it without seeding layer. Dark and photo conductivity of μc-Si showed in the order of 10^{-8} and 10^{-6} S/cm, respectively and optical stability was more improved than a-Si:H layer. Activation energy of μc-Si shows 0.49eV in similar to ideal Si

6. Acknowledgements

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7. References

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