Characteristics of fluoride/glass as a seed layer for microcrystalline silicon film growth

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Abstract

Various fluoride films on a glass substrate were prepared and characterized to provide a seed layer for crystalline Si film growth. The XRD analysis on CaF_2/glass illustrated (220) preferential orientation and showed lattice mismatch less than 5 % with Si. We achieved a fluoride film with breakdown electric field of 1.27 MV/cm, leakage current density about 10^{-6} A/cm^2, and relative dielectric constant less than 5.6. This paper demonstrates microcrystalline silicon (μc-Si) film growth by using a CaF_2/glass substrate. The μc-Si films exhibited crystallization in (111) and (220) planes, grain size of 700 Å, crystalline volume fraction over 65 %, dark- and photo-conductivity ratio of 124, activation energy of 0.49 eV, and dark conductivity less than 4×10^{-7} S/cm.

Introduction

This paper focused on a seed material that can provide the same surface nature as crystalline silicon (c-Si). The seed materials make it possible to grow μc-Si films at a low substrate temperature. Fluoride films such as calcium fluoride (CaF_2), srtrontium fluoride (SrF_2), and barium fluoride (BaF_2) have the same crystal structure and illustrate close the lattice constant as in c-Si. These characteristics of fluoride films were exploited to provide a seed layer for μc-Si film growth. Fluoride films also exhibited ultra-high transmittance in visible spectrum range, which may contribute to improve aperture ratio of TFT-LCD. For a direct μc-Si film growth, fluoride films should meet the following requirements of (1) low lattice mismatch with c-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. This paper presents material properties of the fluoride/glass structure to satisfy the prior mentioned conditions. This paper probes the best seed layer candidate among the various fluoride materials and then applied the optimized seed layer in a direct μc-Si film growth at a low substrate temperature.

Experimental procedure

We carried out experimental investigations starting from fluoride/glass to determine which of the fluorides fits for a seed layer. We deposited 2000 Å thick aluminum as a bottom electrode of metal/fluoride/metal (MFM) capacitor. Fluoride films were grown by thermal evaporation at a base pressure of low 10^{-6} Torr. Pallet-type fluoride sources (3~5 mm) with purity higher than 99.95 % were used in the film growth. To prevent an explosive evaporation of polyatomic cluster we employed a baffled-furnace-type Mo boat for fluoride film growth. The sizes of MFM capacitor were ranged between 2.83×10^{-3} and 7.85×10^{-3} cm^2. Investigated conditions of fluoride films are substrate temperature ranged from room temperature (RT) to 400 °C, growth rate between 0.05 Å/sec and 0.25 Å/sec, film thickness from 500 Å to 1.6 μm, and rapid thermal anneal (RTA) effect. Having structural and electrical properties, we studied a deposition of μc-Si film on CaF_2/glass substrate using a remote plasma CVD (RPCVD) system. Diluted silane gas (20% SiH_4 in He) decomposition was carried out by He^+ ions in this work. The optimized RPCVD process conditions were fixed as RF power of 50 W, temperature 300 °C, chamber pressure 88 mTorr, and SiH_4/H_2 ratio 1.2 %. Using the optimized process parameters, μc-Si films were grown with and without fluoride seed layer to compare the effect of CaF_2 films. Atomic force microscope (AFM) and scanning electron microscope (SEM) were employed for surface morphology study. Crystallographic properties were characterized using a X-ray diffraction (XRD) system of Mac Science M18XHF-SRA with an input power of 40 kV. In XRD study the samples were investigated for a two-theta angle ranged from 20 to 70 degree with a scanning speed of 8.0 deg./min. Raman spectroscopy (Jobin Yvon/T64000) with 400mW Ar laser was employed to determine a crystalline state and crystallized volume fraction of μc-Si film. Electrical properties of fluoride films were evaluated by using Keithley 617, Fluke 5100B, HP 4192A impedance analyzer, and computer data acquisition system. The electrical properties were analyzed in conjunction with structural properties of fluoride.

Results and Discussion

XRD results on a various fluoride films on glass substrate are illustrated in Fig. 1. Most of the investigated fluorides except MgF_2 films exhibited polycrystalline nature starting from a low substrate temperature of RT.

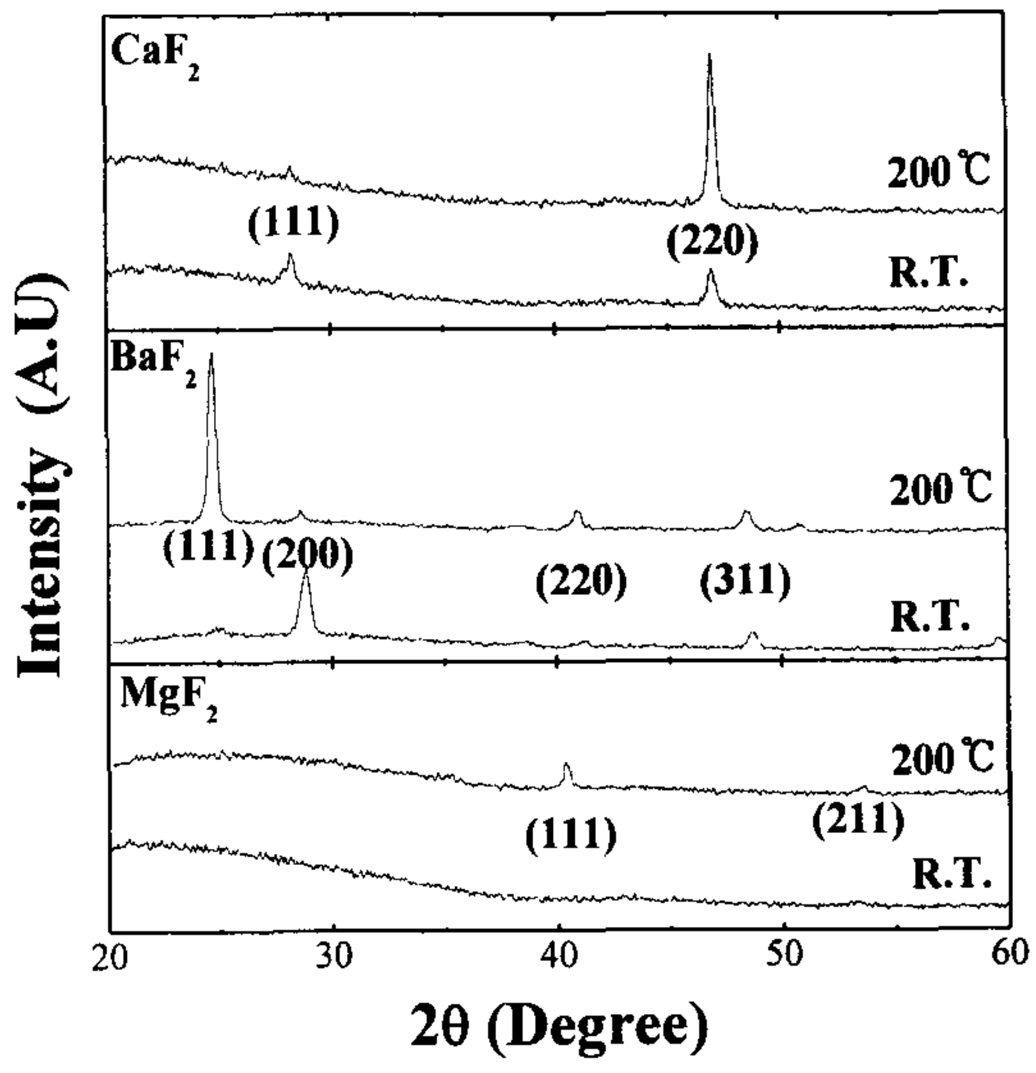

Fig.1. XRD results on fluoride/glass structure.

CaF_2 XRD peaks in Fig. 1 appeared at the same position as in Si film case. Calculated lattice constants of CaF_2 by using a Cohen method showed 0.5459 nm which correspond to 5 % lattice mismatch with Si. The percentage of XRD peak intensity for a randomly oriented powder form fluoride is given as 100 % for

(220), 93 % for (111), and less than 1 % for (200). Because CaF_2 films exhibited the lowest lattice mismatch with Si, we think that (220) preferred CaF_2 films can be useful for large area device applications such as TFT-LCD. SEM and AFM were employed in surface morphology studies of fluoride/glass structure. For the substrate temperature of RT, 100 °C, and 200 °C, we observed average roughness decrease from 54.1 Å to 20.4 Å and 8.40 Å, respectively. Because of the smooth surface morphology is obtained at the increased substrate temperature, we recommend an elevated process temperature where the surface roughness is critical.

We investigated electrical characteristics of fluoride films in terms of growth temperature, film thickness, and different type of material. Among the investigated MFM capacitors, we learn that CaF_2 and SrF_2 film can have a breakdown electric field (E_{br}) higher than 1MV/cm. CaF_2 film grown at RT exhibited a higher E_{br} of 1.27 MV/cm and leakage current density (J_{leak}) around 10^{-6} A/cm^2. Electron energy dispersive spectroscopy analysis on RT grown fluoride films indicated a small amount of Ca-rich compositions with an internal concentration ratio of Ca/F=0.559. The excess Ca may have contributed to increase the leakage current of CaF_2 films with increased donor carriers. J_{leak} and E_{br} characteristics of SrF_2 film as a function of substrate temperature are shown in Fig. 2. For SrF_2 growth temperature at 300 °C, we observed four conduction mechanisms at various bias regions. We interpret the result may have caused by grain boundary effect of SrF_2 MFM capacitor. Whereas, the SrF_2 MFM capacitors fabricated at a low temperature exhibited only two major conduction mechanisms because of less grain boundary effect. E_{br} around 1.02 MV/cm and J_{leak} in the order of 10^{-6} A/cm^2 at an electric field of 500 kV/cm. Generally, a good MFM capacitor demonstrated the breakdown electric field around 1 MV/cm.

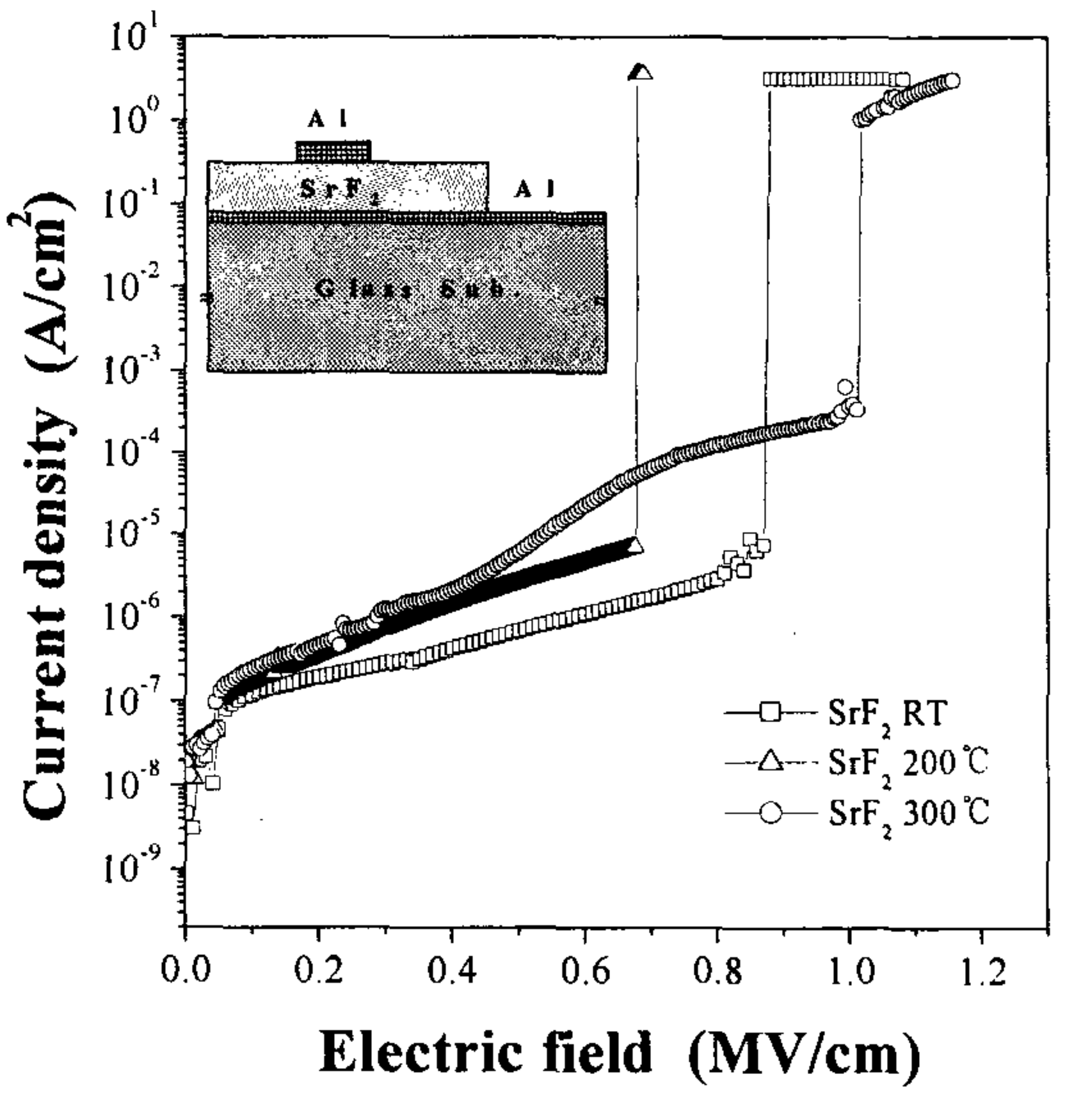

Fig. 2. I-V characteristics of SrF_2 MFM capacitor.

Because CaF_2 meets seed layer requirements, we placed a CaF_2 seed layer on glass substrate and then deposited µc-Si films. RPCVD process conditions were fixed to the optimized proces condition of thin film Si as RF power of 50 W, temperature 300 °C, chamber pressure 88 mTorr, and SiH_4/H_2 ratio 1.2 %. Using the Raman spectroscopy and XRD, we evaluated crystalline structure of thin film Si with and without a CaF_2 seed layer grown at 200 °C. Figure 3 illustrates Raman spectroscopy of µc-Si/CaF_2/glass, a-Si:H/SiO/glass, and c-Si. Raman shift peak appears at 480 cm^{-1} for a-Si:H 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. 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 small grain size we can take the correction factor as unity ($\sigma \approx 1$). Using a CaF_2 seed layer on glass substrate, we were able achieve a µc-Si film with X_c=65 %. XRD study on µc-Si/CaF_2/glass substrate indicates that Si films are oriented to (111) and (220) planes.

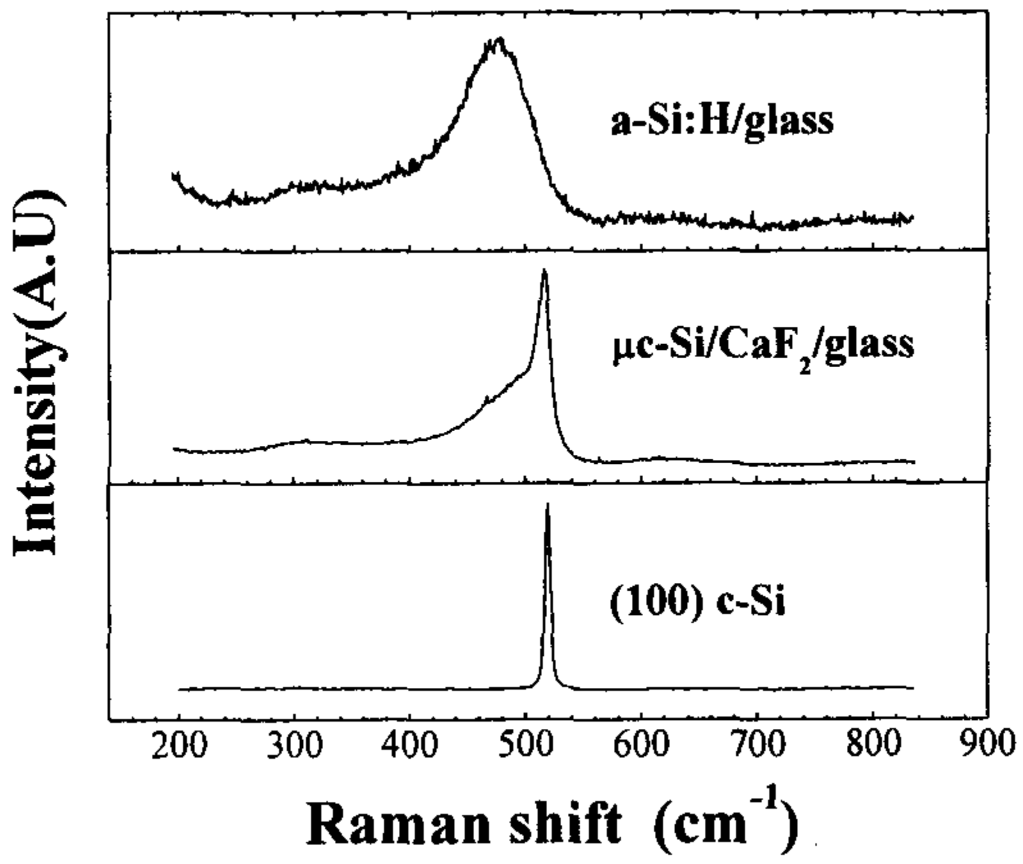

Fig. 3. Effect of CaF_2 seed layer to form µc-Si/CaF_2/glass.

Grain size of thin film Si was determined by SEM illustrated that average grain size is enlarged from 375 Å for a-Si:H/SiO/glass to 700 Å for µc-Si/CaF_2/glass. This result indicates that we can increase the grain size almost twice by replacing a SiO buffer layer with a CaF_2 seed layer. Activation energy which measures carrier transition from intrinsic level to conduction band showed 0.49 eV for µc-Si/CaF_2/glass and 0.76 eV for a-Si:H/SiO/glass. Photoconductivity (σ_{ph}) was measured under the light intensity of 100 mW/cm^2. Photosensitivity of σ_{ph}/σ_d showed 1.08×10^4 for Mg/a-Si:H/SiO/glass and 1.24×10^2 for Mg/µc-Si/CaF_2/glass structure.

Conclusion

We studied various fluoride films on the Corning 1735 glass and determined CaF_2 film as a seed layer for µc-Si film growth. Breakdown electric field around 1 MV/cm and leakage current density less than 10^{-6} A/cm^2 were achieved with CaF_2 MFM capacitors. Employing a CaF_2 seed layer, we achieved µc-Si films with a crystalline volume fraction of 65 %, grain size 700 Å, conductivity higher than 10^{-8} S/cm, σ_{ph}/σ_d about 10^2, and activation energy of 0.49 eV. Our work will stimulate further investigations on a seed material for a direct growth of µc-Si film at a low process temperature and recrystallization of a-Si:H/CaF_2/glass structure.