Interface controlled conduction in a blue-light emitting SrS:Cu, Cl electroluminescent phosphor

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(Received 19 November 1999; accepted for publication 22 March 2000)

The leakage current mechanism of the electron beam evaporated SrS:Cu, Cl films was investigated as functions of electric field and temperature. The activation energy and interfacial barrier height of electronic conduction for Al–SrS:Cu, Cl–In_2O_3:Sn-glass structures were determined by analyzing direct current–voltage characteristics of these structures. We observed in this study that postannealing of the SrS:Cu, Cl films in H_2S atmosphere leads to a reduction of leakage current as well as an increase of interfacial barrier height for the leakage current flowing in these films, regardless of the polarity of applied voltage. On the basis of this observation, we suggest that surface modification induced by the postannealing in H_2S atmosphere may improve the electrical properties of the SrS:Cu films. © *2000 American Institute of Physics.* [S0021-8979(00)01313-X]

I. INTRODUCTION

Many different kinds of thin film phosphors such as SrS:Ce, SrS:Cu, SrS:Cu, Ag, ZnS:Tm, ZnS:Te have been investigated for the application of the blue-light emitting thin film electroluminescent devices (TFELD). Among these materials, the SrS:Cu films have been intensively studied for the blue-light emitting devices and full-color devices and the pure blue chromaticity and high luminance of SrS:Cu and SrS:Cu, Ag make them promising candidates as active layers in thin film electroluminescent devices.[1–6] The light emitting devices based on these materials have demonstrated a luminous efficiency exceeding 0.15 lm/W, which is ease of processing. Owing to an easy oxidation and occurrence of sulfur vacancies, the existence of surface defect centers is easily suspected for the SrS-based films prepared by typical deposition processes.[7–10] It is expected that the SrS:Cu-based devices are very similar to the SrS:Ce-based devices in electrical characteristics. This is a study of the dependence of electronic conduction behaviors through the SrS:Cu films on its deposition processes and film quality. Critical to the development are the understandings of what mechanisms control the current flow at a given operating field, and of how those values of current and field are related to the bulk quality and interface characteristics of the SrS:Cu films.

In this work, we studied the conduction mechanism in the SrS:Cu, Cl films and postprocess dependent conduction properties by taking direct current (I)–voltage (V) as functions of electric field and temperature. For the work, we prepared the electron beam evaporated SrS:Cu+Cl layers which were subjected to two different postanneal treatments: standard-vacuum annealing and H_2S-atmosphere annealing. The dramatic change of interfacial characteristics between bottom (or top) electrodes and SrS:Cu, Cl films with the postprocess was observed and discussed in detail. In this article, we report the conduction characteristics of the indium tin oxide (ITO)/SrS:Cu, Cl/Al structure.

II. EXPERIMENTS

Metal-semiconductor-metal (MSM) structures of glass substrate/ In_2O_3: Sn (ITO)/SrS:Cu, Cl/Al were prepared. The SrS:Cu, Cl (1 mol %) layer was formed by Edwards electron-beam evaporator (E306A) equipped with a Telemark high power E-gun on the Corning 7059 glass substrates coated with ITO with a sheet resistance of about 20 Ω/square. The base pressure in the chamber was below 2×10^{-6} Torr and the substrate temperature was maintained at 300 °C and the thickness varied from 300 to 500 nm in order to examine the bulk effect. During the deposition vacuum pressure was about 2×10^{-6} Torr. The phosphor films on ITO-coated Corning 7059 glass substrate were crystallized by an *in situ* annealing without breaking vacuum. In order to examine the effect of the nonstoichiometric composition or oxidation at the surface, some of the as-deposited films were post-annealed in a H_2S atmosphere at 400 °C for 60 min. The top Al electrodes of 0.7 mm in diameter were formed onto the SrS:Cu/ITO/glass by thermal evaporation at a vacuum pressure of 4×10^{-6} Torr and then the electrical properties of the capacitors with metal–phosphor film–metal structure were characterized. The crystallinity of each film was studied by x-ray diffraction measurement (Rikagu, D/Max-3A). The direct current–voltage characteristics were examined with a

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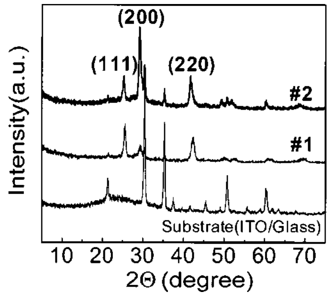

FIG. 1. X-ray diffraction patterns of the films #1 and #2.

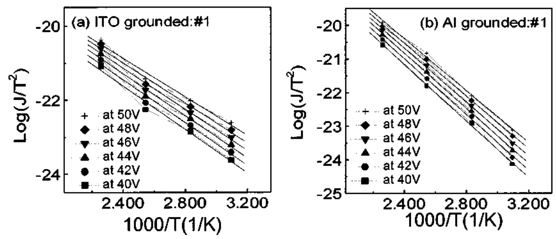

FIG. 3. Plot of log (J/T^2) vs $1000/T$ at near 1 MV/cm for the film #1.

fully automated Keithley 237 high-voltage source with the measuring unit at temperatures ranging from room temperature (RT) to 180 °C.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction (XRD) patterns for two types of 500-nm-thick SrS:Cu, Cl films deposited on ITO-coated glass as well as an ITO coated glass substrate. Sample #1 is the annealed film in vacuum and sample #2 is the annealed film in H_2S atmosphere. The feature of the XRD patterns represents a rock salt structure of the SrS lattice. The strongest peak around 29° due to (200) planes for the 2 is stronger than that of the standard vacuum annealed SrS:Cu, Cl (#1) at 400 °C and this observation indicates the fact that annealing in H_2S atmosphere causes the preferential growth of the (200) planes.

The dc current versus voltage characteristics were examined with the voltage step of 0.5 V/s under the negative polarity, i.e., the negative potential was applied to the bottom ITO electrode. In Fig. 2, one can distinguish a step-like structure followed by a high field region of a relatively fast current increase. This structure of the I–V curve was observed in all SrS:Cu, Cl concerned under this study. At very low fields, the current density (J) increases linearly with the voltage, showing the films' ohmic behavior. The nonlinear behavior at the electric fields exceeding 1 MV/cm can be governed by the space-charge-limited-conduction (SCLC), the Schottky emission, the Poole–Frenkel (PF) emission, or tunneling.

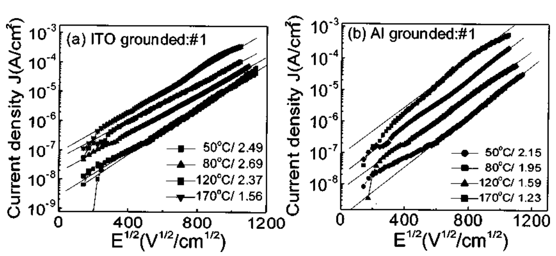

FIG. 2. The polarity dependent J vs $E^{1/2}$ curves for the vacuum annealed (#1) SrS:Cu,Cl thin films. The linearity of log J vs $E^{1/2}$ plot represents the dominant conduction mechanism is the Schottky emission. The onset field of abrupt increase of leakage current is higher as the Al electrode is grounded. The estimated optical dielectric constant deduced from the slopes in these plots is described at the right side of the value of the measuring temperature.

At the field of the order of 1 MV/cm or more, the bulk-limited PF emission and the interface limited Schottky emission will be assumed to the most obvious mechanisms inferring from the linearity of slopes in plotting of Figs. 3(a) and 3(b). In the former case, which is essentially a thermionic emission from a metal electrode into the conduction band of SrS:Cu, the charge carriers, with the image force correction taken into account, are thermally excited over an energy barrier at the ITO-SrS:Cu, Cl interface. This barrier is formed by the equilibrium of the energy of the charge carriers in ITO and SrS:Cu and its magnitude at zero field is modified by the field-dependent lowering of the barrier height due to the image forces. Since both the Schottky emission and PF emission are thermally activated processes, it is necessary to investigate both the field and the temperature dependence of the leakage current in order to determine which of these processes is the operating conduction mechanism.

At first, to prove whether Schottky conduction is the operating conduction mechanism or not, the current dependence of the electric field upon the film thickness is examined here. At a separate measurement, we confirmed the fact that the J–V behavior is independent of the thickness. Furthermore, since there is an asymmetry in the J–V curves for both polarities of the applied voltage, it is tentatively assumed that the conduction is limited by the interface (or electrode). As is well known, in the Schottky conduction the plot of the log (J) as a function of $E^{1/2}$ and log (J/T^2) vs $1000/T$ should be a straight line[11] as shown in Fig. 3 and this is thereby a piece of evidence for the Schottky conduction.

Second, the dielectric constant of the SrS:Cu film is determined from the slope of this straight line in the log $(J)-E^{1/2}$ plot, i.e., β/k_BT,[12,13] to confirm that Schottky conduction in this system is the operating conduction mechanism. In this second method for the confirmation, we took the optical transmission spectra of the film, then estimated the optical refractive index using the Manifacier method. The obtained optical refractive index of the SrS:Cu film is 1.6 and its dielectric constant is 2.6 in the optical frequency region. Of course, the similar magnitude of the dielectric constant from the value based on the Schottky plot can explain the observed J–V characteristics for the SrS:Cu films. Therefore, the two above-mentioned results reveal that the Schottky conduction is the dominant mechanism in our SrS:Cu, Cl films contacted with ITO and Al electrodes in the high field region.

The current dominated by the Schottky conduction depends on the barrier height between metal (ITO or Al)-SrS:Cu, Cl and the barrier height (ϕ_b) depends on the work

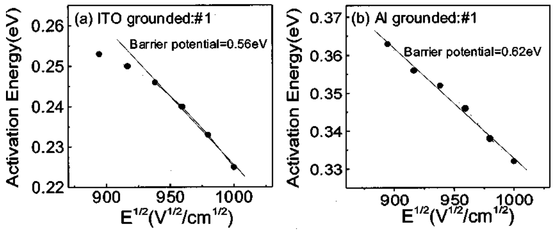

FIG. 4. The polarity dependence of the E_a vs $E^{1/2}$ curve for the #1 SrS:Cu, Cl film.

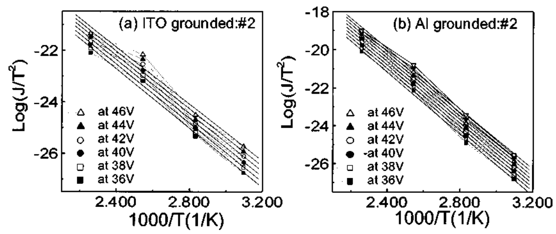

FIG. 6. Plot of log (J/T^2) vs 1000/T at near 1 MV/cm for the film #2.

function of the metal, the barrier lowering by the image force, the surface trap densities, and the surface morphology. Figure 4 shows the activation energies, which were estimated from the slopes in log (J/T^2) vs 1000/T plot and their values are 0.225 and 0.338 eV for the ITO and Al side of the standard vacuum annealed SrS:Cu (#1) at 40 V (0.8 MV/cm), respectively. The potential barrier (Φ_b) for the both interfaces was determined by extrapolating[12] the plots to $V=0$ in Fig. 3. The values of Φ_b at Al (-) and ITO (-) SrS: Cu interfaces are about 0.56 and 0.62 eV, respectively. On the other hand, the decrease of leakage current as well as the increase of onset voltage of abrupt increase of current was observed at #2, as shown in Fig. 5. The values of the activation energy for the ITO and Al sides of the SrS:Cu annealed in H_2S atmosphere in Figs. 6 and 7 are determined to be 0.485 and 0.693 eV at 40 V, and the values of the potential barrier (Φ_b) for the both interfaces was about 0.67 and 0.77 eV.

Now let us explain our observations on the reduction of the leakage current level and on the raising of the interfacial barrier height observed in film #2. We suggest here the decrease of the surface roughness after the H_2S annealing as one of the possible origins for the reduction. Figure 8 shows the images for the top surface of the SrS:Cu films before and after annealing in H_2S ambient and we can see clearly a dramatic change of the topology of the top surface as well as the decrease of hillock density. The root-mean-square roughness probed by the atomic force microscopy from the 20 μm by 20 μm scan was 100.05 and 1.04 nm for the films #1 and #2, respectively. The variation of the surface morphology can be related to the crystallinity of the film and strain existing in the film. The annealing temperature provided to the deposited atoms could increase surface migration and the film with flat surface as well as high crystallinity can be obtained. The effect of annealing temperature is the same for the both films of #1 and #2. So, the surface morphology is a determinant parameter for the reduction of leakage current level for the films #2. Furthermore, for the H_2S annealing effect such as a suppression of the leakage current and increase of interfacial barrier height we should consider the possibility that the origin of the leakage current and lower barrier height for electron injection can be also ascribed to sulfur vacancies existing not in the bulk of SrS but in the surface region near contact areas. When the SrS:Cu film was annealed in H_2S atmosphere at over the deposition temperature, the filling of sulfur vacancies in top surface of SrS easily occurs, resulting in more stochiometric composition. On the other hand, the increase of barrier potential after H_2S treatment at the ITO side may be related to the change of oxygen vacancies, which is a well-known factor determining the conductivity of ITO film. The annealing in H_2S results in the filling of the oxygen vacancies with sulfur atoms, which is accompanied by the increase of the potential barrier.

The interfacial barrier height after H_2S annealing increased as expected. The activation energies in the high temperature and high voltage region correspond to the energy barrier that the electron should overcome to transfer to the ITO/SrS:Cu or Al/SrS:Cu. Therefore, we believe that this increase in the interfacial barrier height at both sides is due to a change in the band alignment, perhaps due to a difference in interface charge states[13] or the strain at the contact interfaces with the postdeposition process.

The observed results suggest that there are two dominant conduction mechanisms for the SrS:Cu, Cl films in the ITO-SrS:Cu–Al structure depending on the magnitude of the electric field; namely an ohmic type at low field region, but at higher fields the conduction is governed not by the field enhanced thermal excitation of charge carrier from bulk traps but by the Schottky emission as a result of the barrier lowering due to the applied field and the image force.

Considering that as-deposited SrS:Cu films without any post-treatment shows Schottky conduction in high field regime, SrS:Cu films follow an intrinsically interface con-

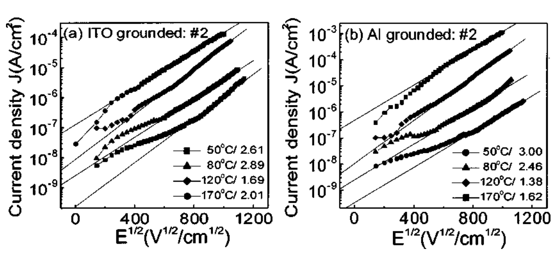

FIG. 5. The polarity dependent J vs $E^{1/2}$ curves for the #2 SrS:Cu, Cl thin film.

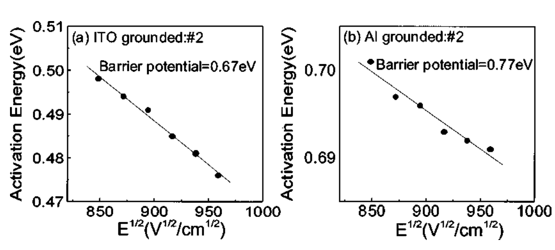

FIG. 7. The polarity dependence of the E_a vs $E^{1/2}$ curve for the #2 SrS:Cu, Cl film.

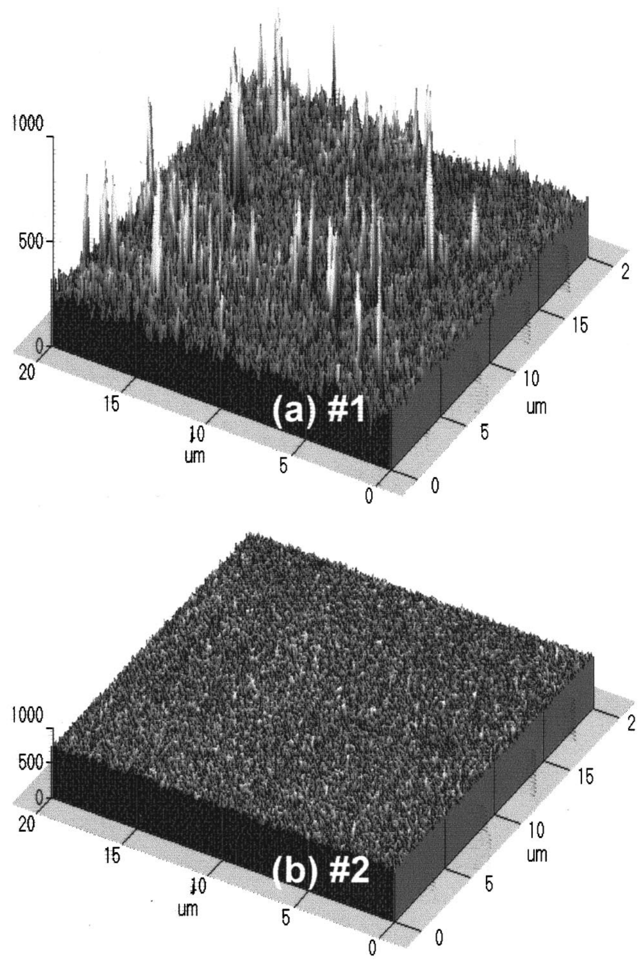

FIG. 8. The typical view of the surface on 500-nm-thick SrS:Cu, Cl films: (a) sample 1 and (b) sample 2. Note the brightest spikes, i.e., hillocks, in (a).

trolled mechanism contrary to bulk limited conduction of ZnS-based films.[14] Therefore, the surface modification induced by the postannealing in H_2S atmosphere seems to work effectively for the reduction of leakage current in this film.

IV. CONCLUSION

The activation energy and interfacial barrier height of Al/SrS:Cu, Cl/ITO/glass capacitors were determined from the analysis of using dc current–voltage characteristics. Both the current–voltage and the current–temperature characteristics of the SrS:Cu films can be fitted well with the Schottky conduction mechanism, which is one of the interface controlled mechanisms. The obtained results indicate that post-annealing in H_2S atmosphere increases both the activation energy for electronic conduction and interfacial barrier, resulting in lower leakage current.

As expected, the annealing in H_2S atmosphere results in more stoichiometric compound resulting a higher crystallinity as well as a dramatically flattened surface topology. Since the high temperature annealing was performed for the both films, we suggest that H_2S annealing contributes to the filling of surface sulfur vacancies and therefore, the change of the surface states near the interface was also one of the main causes for the observed results. Finally, we suggest that the surface treatment and/or modification process may work effectively for the control of the leakage current behavior in this film because the leakage current mechanism of Cu-doped SrS followed mainly the interfacial controlled mechanism.

ACKNOWLEDGMENT

The authors would like to thank Dr. Sang-Sik Kim at Korea University for valuable discussions.

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