Thin Solid Films 519 (2011) 4234–4238

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Electrical insulation and bending properties of SiO_x barrier layers prepared on flexible stainless steel foils by different preparing methods

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ARTICLE INFO

Article history:
Received 21 May 2010
Received in revised form 22 February 2011
Accepted 22 February 2011
Available online 2 March 2011

Keywords:
Silicon oxide
Dielectric barriers
Electrical insulation
Bending resistance
Stainless steel foils

ABSTRACT

Stainless steel foils on which flexible display devices and integrated solar modules are prepared need to be coated by barrier layers for electrical insulation. In this study, SiO_x barrier layer was prepared on steel foils (SUS 304) by ion beam assisted deposition, Sol–gel deposition and plasma enhanced chemical vapor deposition, respectively. The electrical properties of the SiO_x films, such as resistance, reactance, leakage current density, breakdown field strength and performance index were investigated, and the bending properties were evaluated by bending tests. The best electrical insulation and bending properties of barrier could be achieved with 4 μm thick SiO_x layer prepared by plasma enhanced chemical vapor deposition.

1. Introduction

Electronic paper and organic light-emitting diode displays have been extensively developed for the applications to next-generation display devices such as e-books, e-newspapers and cellular phones. Whereas glass has been the principal material for the substrates of conventional display devices, plastic films and metal foils are attracting attention because of their flexibility as the substrates of flexible display devices. Although the plastic films are lightweight, flexible and available in a wide variety, the types of plastic films applicable to thin film transistor (TFT) backplanes are limited because of chemical stability, heat resistance, moisture resistance and so on. For this reason, the plastic films that are presently studied for the application are limited to polyimide, polyether sulphone, polyethylene glycol terephthalate, etc. [1,2]. With respect to metal foils, the suitability of stainless steel foils for the TFT backplane application is being studied and some prototype displays have been produced using stainless steel foils [3–5]. Conventional Si-based TFT backplane process requires temperatures in excess of 300 °C which cannot be tolerated by current plastic substrates, so stainless steel foils with excellent heat resistance were chosen [6,7]. Besides, stainless steel foils are widely used in the field of solar energy for its many advantages compared to plastic films. Solar cell efficiency of $\eta = 12.8\%$ was reported on a 20-μm thin polyimide film [8], and even $\eta = 17.1\%$ could be achieved on stainless steel substrates [9]. For larger size devices, a 8.4% efficiency from $Cu(In_x,Ga_{1-x})Se_2$ solar cells roll-coated onto a stainless steel substrate was realized [10].

Since stainless steel foil is electrically conductive and its surface is rougher than that of glass substrate, it is necessary to deal with the surface as coated with a barrier layer. The barrier has two functions: (a) to provide electrical insulation between the metal substrate and the monolithically interconnected cells; and (b) to reduce the diffusion of impurities from the metal substrate into the above functional layers. Herz et al. reported that the best insulating barriers could be achieved with 6-μm thick composited layers of SiO_x (plasma enhanced chemical vapor deposition, PECVD for short, 3 μm)/SiO_x (Sol–gel, 3 μm) or SiO_x (PECVD, 3 μm)/Al_2O_3 (sputtered, 3 μm) [11]. Kessler et al. reported that a suitable SiO_x dielectric barrier was obtained by PECVD on a titanium metal foil [12]. Yamada et al. reported that an insulating film of organically modified silicate with a thickness of 1.5 μm on a stainless steel foil by the Sol–gel process had an insulating resistance as high as 10^9 Ω cm^2 [13]. However, there have been few reports on bending properties of barriers, and comparisons of electrical insulation and bending properties of the barriers prepared by different fabrication methods. In this paper, ion beam assisted deposition (IBAD), Sol–gel deposition and PECVD were adopted to prepare SiO_x barrier layers on stainless steel foils, and the electrical insulation and bending properties of SiO_x were compared.

2. Experimental details

The flexible stainless steel foils (SUS 304, 150 μm) were adopted in this experiment without deep scratches and rolling traces, so that

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0040-6090/$ – see front matter
doi:10.1016/j.tsf.2011.02.075

all inhomogeneities can be covered by the SiO_x barrier layer. Surfaces of the steel foils were pre-treated by mechanical polishing and electrolytic polishing as our previous work, and the surface medium roughness (R_a) and maximum roughness (R_t) were 1.7 nm and 19.38 nm, respectively [14,15].

The ZZSX-800ZA automatic vacuum coating machine was adopted in this experiment. The substrates were cleaned with commercial detergent and deionized water before loading. Prior to deposition, the substrates were pre-cleaned using Ar^+ ion beam bombardment for 5 min in order to further reduce impurities on the substrate surfaces. The Ar^+ ion beam parameters for cleaning are: ion energy of 350 eV, ion beam current of 100 mA and argon flux of 5 sccm [16,17]. The parameters of SiO_x prepared by IBAD are: ion energy of 330 eV, ion beam current of 100 mA, argon flux of 6 sccm, evaporation rate of 0.6 nm/s, preparing vacuum of 9×10^{-3} Pa, temperature of 30–45 °C [16,17].

Sol–gel deposition was carried out in this experiment. The solution consisted of tetraethoxysilane (TEOS), ethanol (EtOH) and H_2O (the molar ratio: TEOS:EtOH:H_2O = 4:27:1), and 0.01 mol/L hydrochloric acid and ten millionths (molar ratio) of N, N-dimethylformamide were used as the catalyst and chemical additive respectively, to overcome the thermal stress in the annealing process. A stirrer was used to churn the solution for 3 h, and then the solution was put aside at room temperature for 3 days. Lastly, a piece of quantitative filter paper was adopted to filter the solution. The film preparation procedure was as follows: firstly, a spin coating machine with a speed of 3500 r/min was used to gain a uniform "wet film" on a steel foil (60 mm × 60 mm). Secondly, the "wet film" was put in an oven at 100 °C for 24 h to evaporate the water and organic matters to gain a "dry film". Finally, a dense film of SiO_x was formed by sintering the samples at 500 °C in air for 1 h at the speed of 2 °C/min.

Oxford Plasmalab System 100 was adopted in this experiment. The parameters of SiO_x prepared by PECVD are: SiH_4 flux of 30 cm^3/min, N_2O flux of 300 cm^3/min, He flux of 250 cm^3/min, power of 150 W, temperature of 270 °C and pressure of 106 Pa. The film thickness of SiO_x prepared by the above three preparing methods was in the range of 1–5 μm, which was recalibrated by post-deposition ellipsometry measurements (VASE, J.A. Woollam Co., Inc.).

The insulation resistance R_d, reactance R_c, leakage current density J, breakdown field strength E_{BD} and performance index Q_{BD} of the SiO_x barrier layers were measured to characterize the electrical insulation properties. For this purpose, 90 Cu contacts with a diameter of 1 mm were deposited through a Ti mask onto the barrier-coated steel foils, and the data were averaged to characterize the electrical insulation properties of SiO_x barrier layers. Cu contacts were prepared by the IBAD, and the processing parameters are: ion energy of 350 eV, ion beam current of 80 mA, argon flux of 6 sccm, evaporation rate of 0.8 nm/s, preparing vacuum of 9×10^{-3} Pa. A Keithley 2400 ammeter was used to measure the leakage current density, and a programmable automatic RCL meter (FLUKE PM6304) was adopted to measure the resistance, reactance and permittivity of barrier layers (frequency f = 1000 Hz, voltage U = 2 V). Besides, a DH1722A-5-type DC stabilized power supply was used to test the breakdown field strength of barrier layers. The testing geometry for electrical insulation properties of SiO_x barrier layers is shown in Fig. 1.

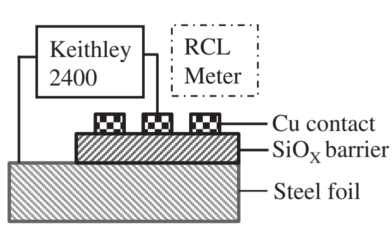

Fig. 1. Testing geometry of SiO_x barriers.

The experimental program of evaluating bending properties of SiO_x barrier layers is shown as follows [13]: the stainless steel foils coated with SiO_x barrier layers and Cu electrodes were subjected to 500 cycles of outward or inward bending around a cylinder with variable radius (R = 15 mm, 25 mm, 35 mm). After the bent specimen foils were flattened, the insulation resistance was measured by applying a direct current voltage of 30 V between the Cu electrodes and the steel foil, as shown in Fig. 1. The bending properties of SiO_x barrier layers were evaluated by an insulation ratio of N/90, N being the number of the Cu electrodes where the insulation resistance was 10^8 Ω cm^2 or higher.

3. Results and discussion

3.1. Electrical insulation properties of SiO_x barriers

3.1.1. Impedance of SiO_x barriers

Under alternating current measuring mode, the impedance of SiO_x barrier consists of resistance and reactance ($Z = R_d + iR_c$). The resistance and reactance of SiO_x barriers deposited by IBAD, Sol–gel and PECVD are shown in Fig. 2 (a) and (b), respectively. From Fig. 2 (a) and (b), we can see that the resistance and reactance of SiO_x barriers prepared by IBAD, Sol–gel and PECVD basically increase in a linear function with the increasing thickness, and the resistance and reactance of SiO_x prepared by PECVD are higher by 2–3 orders of magnitude than the ones by the other two methods. We can also conclude that the resistance and reactance of SiO_x prepared by IBAD

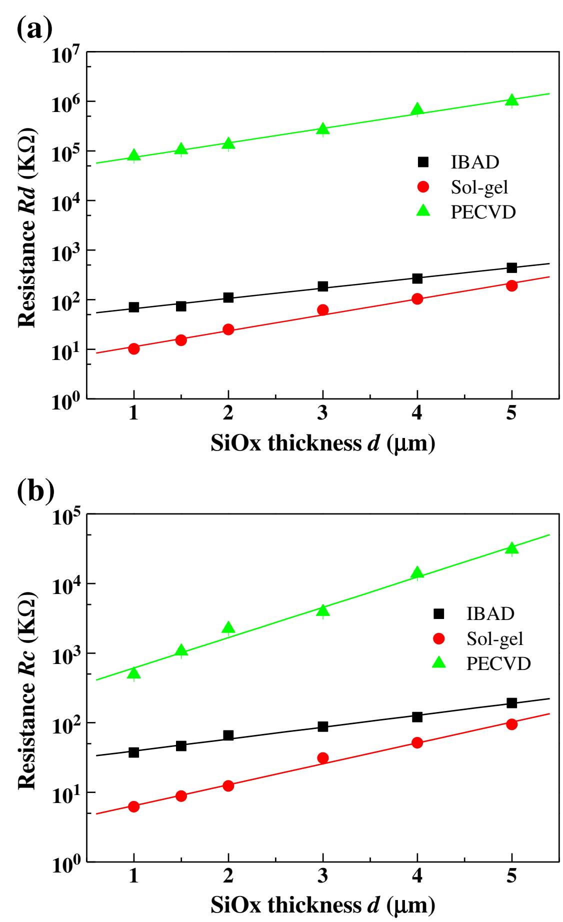

Fig. 2. Relationships between impedance and thickness of SiO_x barriers: (a) Resistance and (b) reactance. The data were measured 5 times and treated by averaging, and mean square root error (MSRE) of the data as the error bar, but the value is too small to see in the chart.

are higher than the ones by Sol–gel at the same thickness. By comparing the resistance or reactance of all SiO_x, it is indicated that PECVD, compared to the other two preparing methods, could prepare SiO_x with higher impedance. The reasons are as follows: (1) the SiO_x films prepared by PECVD are more dense and smooth compared to Sol–gel, as shown in Fig. 3 AFM images, and few pin-holes, impurities and defects in film occur. The SiO_x films prepared by Sol–gel often show cracks and delamination after sintering at $T \geq 500\,°C$ [11], as shown in Fig. 3 SEM images; (2) the conformation of SiO_x film prepared by IBAD is a columnar + hole structure, and the ion bombardment of ion source will result in the production of more pin-holes. Thus, the SiO_x film prepared by IBAD has more pin-holes and defects than one by PECVD process.

3.1.2. Leakage current density of SiO_x barriers

The relationships between leakage current density J and field strength E of SiO_x barriers prepared by three different methods are shown in Fig. 4 (a) and (b). The barrier thickness in Fig. 4 (a) and (b) was 3 μm and 4 μm, respectively. Under the same field strength, the leakage current density of SiO_x prepared by PECVD was lower by 2–3 orders of magnitude than ones by the other two methods. When the field strength $E = 0.2$ MV cm^{-1}, the leakage current density of SiO_x barriers (3 μm) prepared by PECVD was $J = 4.7 \times 10^{-6}$ A cm^{-2}, but the ones of Sol–gel and IBAD were $J = 1.7 \times 10^{-3}$ A cm^{-2} and $J = 3.4 \times 10^{-4}$ A cm^{-2}, respectively. As shown in Fig. 4 (b), the leakage current density does not respond linearly to the field strength when the SiO_x barriers are 4 μm. The reason for this is the effect of the field strength on the leakage current density is less sensitive for the dense SiO_x films. Thus, the requirement of low leakage current density of SiO_x prepared by various methods could be met while the thickness is in the range of 3–4 μm.

3.1.3. Breakdown field strength and performance index of SiO_x barriers

SiO_x barrier samples prepared by three fabrication methods were selected in this experiment, and all the film thickness were kept the same as $d = 500$ nm. The breakdown voltage (U) of SiO_x barrier is defined as the voltage at which the current increases sharply. The breakdown field strength (E_{BD}) was calculated according to the following formula: $E_{BD} = \frac{U}{d}$, and the data were treated by averaging. The results are shown in Table 1.

From the above data we can know that the E_{BD} of SiO_x prepared by PECVD is the highest, basically close to the intrinsic breakdown field strength (6 MV/cm), which indicates perfect quality of the SiO_x prepared by PECVD process. That is because few pin-holes, impurities and defects occur in the film, and non-intrinsic breakdown takes place rarely. The E_{BD} of SiO_x prepared by Sol–gel is the lowest for its cracks, defects and loose structure, and most of the breakdown is non-intrinsic.

The critical charge density or electric displacement when the dielectric films are broken down is called the performance index (Q_{BD}) of dielectric films, which is equal to the product of permittivity (ε) and breakdown field strength (E_{BD}) $Q_{BD} = \varepsilon \times E_{BD} (\varepsilon = \varepsilon_r \varepsilon_0)$. Performance indices of SiO_x barriers prepared by different methods are also shown in Table 1.

From Table 1 we can conclude that the Q_{BD} of SiO_x prepared by PECVD is the highest and the Q_{BD} of SiO_x prepared by Sol–gel is the

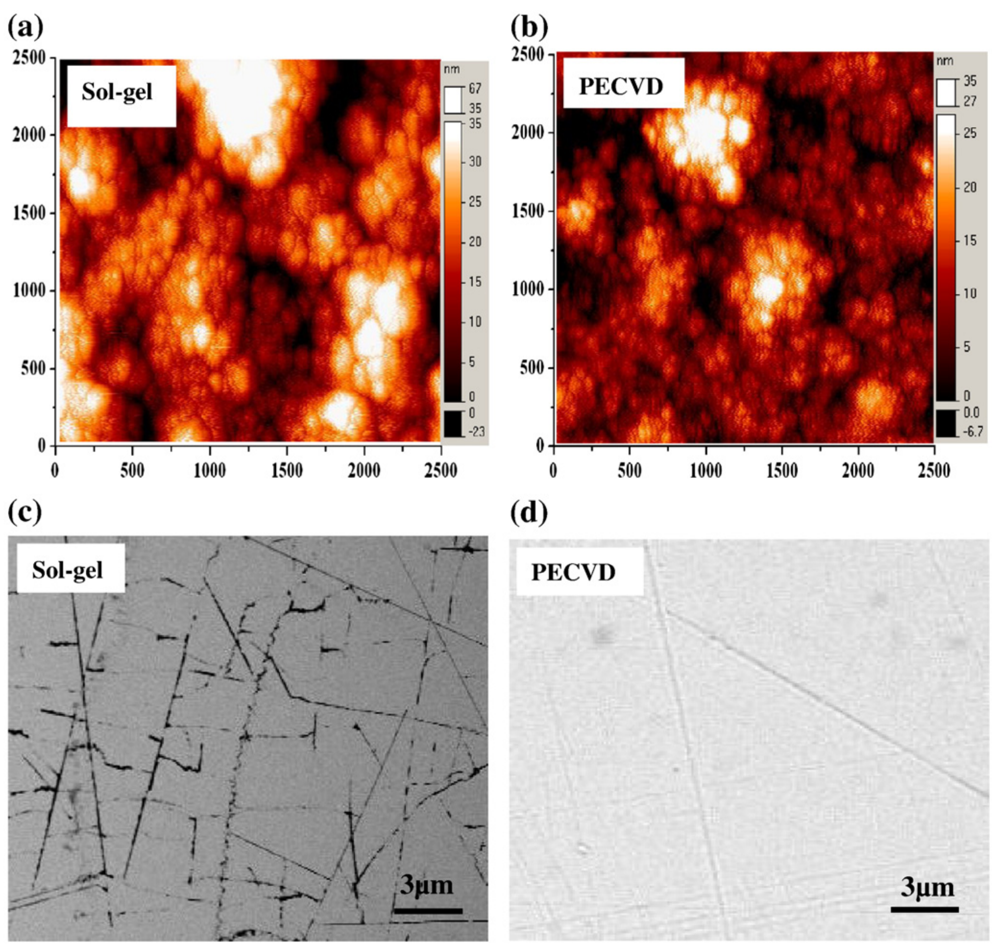

Fig. 3. AFM and SEM images of SiO_x barriers prepared by Sol–gel and PECVD.

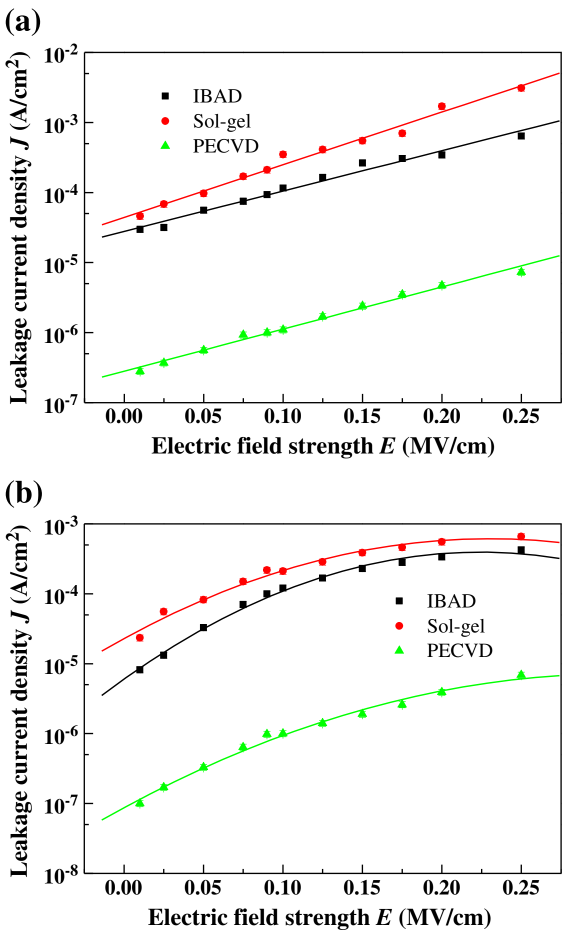

Fig. 4. Relationships between leakage current density J and electric field strength E of SiO_x barriers prepared by different methods at different thickness: (a) 3 μm and (b) 4 μm. The data were measured 5 times and treated by averaging, and mean square root error (MSRE) of the data as the error bar, but the value is too small to see in the chart.

lowest. To summarize, the comprehensive properties of permittivity and breakdown field strength of SiO_x prepared by PECVD is the best.

3.2. Bending properties of SiO_x barriers

When the SiO_x barriers are bent inward or outward, the corresponding insulation ratio under different bending radius is shown in Fig. 5 (a) and (b), respectively.

From Fig. 5 (a) we can see that the insulation ratio of SiO_x prepared by PECVD is the highest and one of the Sol–gel deposition is the lowest, when the films were bent inward. This illustrates that the SiO_x prepared by PECVD has good bending properties, while Sol–gel deposition is unsatisfactory. As the bending radius R increases, the insulation ratio of all SiO_x increases gradually, and the insulation ratio of SiO_x prepared by PECVD is up to 100% at $R \geq 25$ mm. The results from Fig. 5 (b), when the films were bent outward, are similar with ones from Fig. 5 (a), except that the SiO_x prepared by PECVD obtains 100% insulation ratio at $R \geq 35$ mm. The different thresholds bending

Table 1
Breakdown field strength and performance index of 500-nm thick SiO_x barriers made using different preparation methods.

Preparing methods	PECVD	IBAD	Sol–gel
Breakdown field strength	5.72 MV/cm	4.86 MV/cm	4.17 MV/cm
Performance index	1.83 μc/cm^2	1.70 μc/cm^2	1.67 μc/cm^2

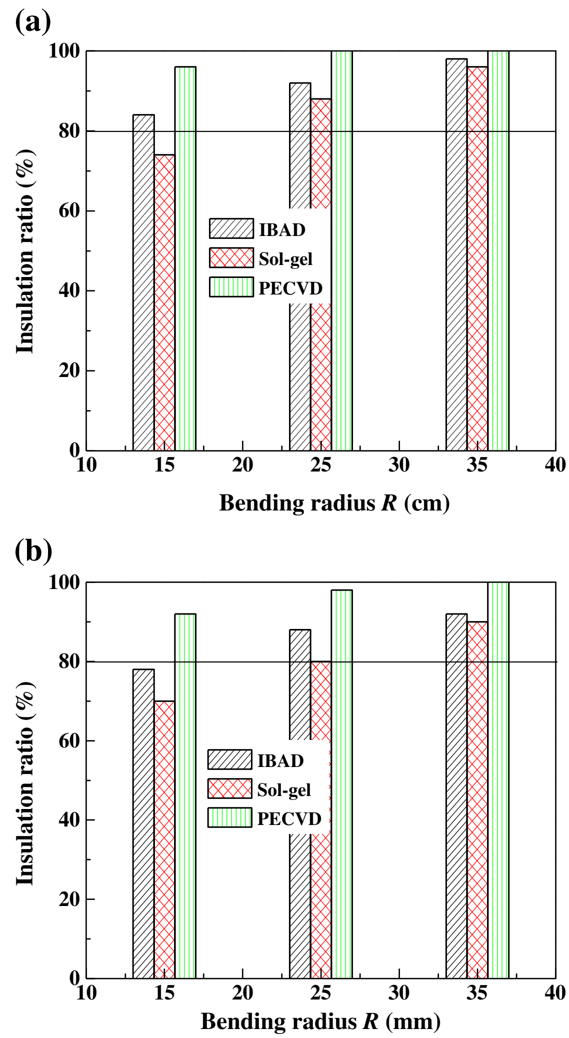

Fig. 5. Relationships between bending radius and insulation ratio of SiO_x barriers: (a) inward bending and (b) outward bending.

radius for 100% insulation ratio indicate that the bending properties of SiO_x subjected to inward bending are better than those subjected to outward bending under the same bending radius. The reasons are as follows: (1) all SiO_x prepared by different fabrication methods show a tensile stress, and the SiO_x films have a shrink trend compared to the steel foils [18–21]; (2) the tensile stress resulted from outward bending is easier to cause SiO_x films to be damaged, which result in the formation of cracks.

4. Conclusion

It is a great challenge to obtain perfect electrical insulation and bending properties of barrier layer for the preparation of functional modules on metal substrates. In this paper, IBAD, Sol–gel and PECVD were adopted to prepare SiO_x barrier on stainless steel foils. It was found that the electrical insulation and bending properties of SiO_x barrier prepared by PECVD is better than those of the other two preparing methods. Stainless steel foils coated with SiO_x barriers by the PECVD method demonstrated excellent electrical insulation and bending resistance properties. High barrier resistance of $R_d > 40$ MΩ, high breakdown field strength of $E_{BD} > 5$ MV/cm and low leakage current density $J < 10^{-5}$ A cm^{-2} could be achieved by PECVD. The bending properties of SiO_x subjected to inward bending are better than those subjected to outward bending under the same bending radius. Results of J–E measurements demonstrated the effectiveness of SiO_x barriers and the potential for further progress. The stainless steel foil with an insulating film is highly promising as the material for the substrates of flexible display devices and solar cell.

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