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Influence of deposition pressure and power on characteristics of RF-Sputtered Mo films and investigation of sodium diffusion in the films

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Mo films deposited by DC sputtering are widely used as back contact in CIGS and CZTS based thin film solar cells. However, there have been only a few studies on the deposition of Mo films by RF sputtering method. In this context, Mo films on SLG substrates were prepared as a function of deposition pressure and power by using RF magnetron sputtering method to contribute to this shortcoming. Mo films were deposited at 250 °C substrate temperature by using 20, 15, 10 mTorr Ar pressures at 120 W RF power and 10 mTorr Ar pressure at 100 W RF power. Structural, morphological and reflectivity properties of RF-sputtered Mo films were clarified by XRD, AFM, FE-SEM and UV–Vis measurements. In addition, due to sodium incorporation from SLG substrate to the absorber layer through Mo back contact layer is so essential in terms of improving the conversion efficiency values of CIGS and CZTS thin film solar cell devices, the effects of Na diffusion in the films were analyzed with SIMS depth profile. The electrical properties of the films such as mobility, carrier density and resistivity were determined by Hall Effect measurements. It was found that Mo films prepared at 120 W, 10 mtorr and 250 °C substrate temperature and then annealed at 500 °C for 30 min, had resistivity as low as 10^{-5} Ω cm, as well as higher amount of Na incorporation than other films.

1. Introduction

Molybdenum (Mo) films have been attracted much attention in many various technological areas due to remarkable properties of Mo material such as high mechanical hardness, high thermal stability and high electrical conductivity [1]. They are used as diffusion barriers in microelectronics [2], as protective films in high temperature applications [3], as interconnect material in very large scale integrated circuits [4] and in thin film transistor displays [5]. However, Mo films are most widely used as back contact in CIGS [6], CdTe [7] and CZTS [8] thin film solar cell devices. Although several materials such as Au, W, Pt, Ni, Al, Ag, Cr and Ti have been investigated as back contact, compared to the other materials Mo is the most ideal material for CIGS and CZTS based thin film solar cells [9–14]. The main properties of Mo films such as high conductivity, low resistance contact with the absorber layer, good adhesion on the soda lime glass substrate, good chemical and heat inertness during the growth of absorber layer and high temperature selenization and sulfurization processes of the cell production make them a preferred back contact choice in thin film solar cells researches [6,9,15]. So far the highest conversion efficiency cells have yielded by using Mo back contacts for CIGS and CZTS thin film solar cell devices [16,17]. On the other hand, Mo back contact enables sodium (Na) diffusion from soda lime glass (SLG) substrate through the Mo layer into the absorber layer in CIGS and CZTS thin film solar cell devices. The diffusion of Na element into the absorber layer depends on deposition parameters of the Mo back contact strongly [18]. In our previous work, structural, morphological and electro-optical properties of RF-sputtered Mo films were systematically investigated as depending on the deposition and annealing temperatures [19]. However, there are still some open points in the literature about producing of Mo back contact films for electro-optical devices having high conductivity and high optical

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reflectance as well as controllable Na diffusion from SLG substrate as depending on deposition parameters such as working pressure and sputter power.

Several techniques can be used to obtain Mo films such as DC [6,12,20] or RF magnetron sputtering [21–23], chemical vapor deposition [24], ion-beam assisted deposition [25,26], e-beam evaporation [27,28] and laser ablation deposition [29,30]. Among these techniques, magnetron sputtering is a leading technique for the deposition of Mo films. It has some advantages compared to the other techniques such as scalability to large areas, homogeneity over large areas, reproducibility and very good stability. Many researches have been done over the deposition of molybdenum films by DC sputtering [10,15,20,31]. However, there have been no many works on RF sputtered Mo films [21–23]. Therefore, it is important to find out RF sputtered Mo films' properties in terms of being an alternative method for developing and expanding CIGS and CZTS thin film solar cells technologies. In RF magnetron sputtering method, an alternating voltage, which oscillates at radio frequency (13.56 MHz), is applied to the target material. By this way, the possible arching in the plasma is reduced and it gets easier to keep plasma going compared to DC sputtering [32]. In addition, the working pressure of deposition can be decreased to much lower values without breaking the plasma in RF sputtering technique and this provides to obtain Mo films with less undesired impurity, which is coming from argon gas [21].

Moreover, it is well known that the deposition parameters like sputtering power, Ar gas pressure and substrate temperature play an essential role on the formation of a Mo back contact layer with the suitable properties in sputtering technique. The structural, morphological, electrical and optical properties of molybdenum films change considerably as a function of these deposition parameters. Particularly, there has been a strong correlation between the kinetic energy of the sputtered molybdenum atoms and the Ar gas pressure. As a result of this, the Mo films had different microstructure, electrical conductivity and adherence can be obtained by changing working gas pressure. The Mo films sputtered at high Ar pressures show tensile stress and have a porous microstructure. Although these kinds of films adhere to the substrate well, they have high resistivity. On the other hand, the films sputtered at low Ar pressures exhibit compressive stress with dense microstructure because of the high kinetic energy of atoms reached to the substrate and this case results in poor adherence to the substrate and low resistivity [33–37].

The aim of this study is to investigate the structural, morphological, electrical and optical properties of RF sputtered Mo films depending on critical deposition parameters such as Ar gas working pressure and RF sputtering power and to obtain a back contact with good adherence and low resistivity for solar cells. Another important motivation of the study is to find out the behavior of the Na diffusion mechanism in Mo films depending on deposition parameters by SIMS analysis.

2. Experimental

Mo films were deposited on $30 \times 50 \times 1.2\ mm^3$ SLG substrates by radio frequency (RF) magnetron sputtering of a 99.95% pure Mo target (2" dia × 0.250" thick) in a sputtering system with confocal geometry (Nanovak, NVTS500). The SLG substrates were firstly cleaned in soapsuds by the help of a sponge and then they were rinsed in distilled water. After this first cleaning step, the substrates were cleaned in an ultrasonic bath containing soapsuds for 5 min and subsequently rinsed with the distilled water again. Lastly, they were blow-dried with nitrogen gas and introduced into the sputtering chamber. Before the deposition process, the base pressure of sputtering chamber was approximately evacuated to 10^{-7} Torr. The distance between target and substrate was 12 cm with a 45° angle to the substrate and the substrate holder was rotated at 8 rpm with the aim of depositing homogeneous film. The Ar gas flow rate was changed according to the working pressures of the deposition processes as 6.8 sccm for 20 mTorr, 5 sccm for 15 mTorr and 3.1 sccm for 10 mTorr. At the beginning of each deposition process, the targets were pre-sputtered for 8 min for the purpose of cleaning by Ar plasma.

In this work, two series of Mo films were prepared under different sputtering conditions. In the first series, the Mo films were deposited at 250 °C substrate temperature by using 20, 15, 10 mTorr Ar pressures at 120 W RF power (M1, M2 and M3) and for this series, another Mo film was re-sputtered in the same condition as previous one at 10 mTorr Ar gas pressure, then it was annealed under Ar gas atmosphere in the deposition chamber at the temperature of 500 °C for 30 min (M4). In the second series, Mo films were deposited by applying 100 W RF power at 10 mTorr Ar gas pressure at 250 and 350 °C substrate temperatures (M5 and M6). All deposition parameters of the films were listed in Table 1. The thicknesses of the deposited Mo films were determined by a stylus type profilometer (Veeco, Dektak 150). The crystalline structure of the films was examined by X-ray diffraction (XRD, APD 2000 PRO diffractometer) in a 2θ range of 20°–90° with CuKα radiation (λ = 1.54052 Å). The optical reflectance of the Mo films was measured by using Perkin Elmer Lambda 2 S UV–Vis Spectrometer in the wavelength range of 200–1100 nm. Room-temperature electrical resistivity, carrier mobility and carrier density of the films were characterized by the van der Pauw technique using Lake Shore Hall-effect Measurement System. Surface morphologies of Mo films were studied by field-emission scanning electron microscopy (FE-SEM) (FEI Quanta-400 F) with an acceleration voltage of 20 kV and atomic force microscopy (AFM) (hpAFM, NanoMagnetics Instruments) using dynamic mode scanning at room temperature. The sodium distribution in Mo films was analyzed by secondary ion mass spectroscopy (SIMS) (Hiden Analytical Ltd., Warrington, UK). The SIMS measurements were performed by using a primary ion beam of O_2 (oxygen) ions with 3850 eV energy. The primary ion current was 400 nA for the O_2 beam. The secondary ions were collected from an area of $100\ \mu m^2$. For all measurements, the base pressure of the chamber was kept at 10^{-10} mbar. The sputtering depth was determined from SIMS crater depth by using the stylus profilometer.

3. Results and discussion

The adhesion test of the Mo films deposited on SLG substrate was performed by a scotch tape based on ASTM standard D3359-09. All the films in this study had good adhesion to the SLG substrates. It was determined by profilometer measurements that Mo films were obtained with different thicknesses of 933, 961, 966, 1134, 1221 and 1391 nm depending on the growth rate (Table 1).

Fig. 1 shows the XRD patterns of the Mo films deposited at various Ar pressures and RF powers. For all films, the most intense peak was obtained at the range of $2\theta = 40.82°$ - 40.97° with a preferred orientation along the (110) direction which is attributed to Mo's body centered cubic (BCC) structure (JCPDS Card No. 42-1120). In addition, it was seen that all Mo films had a narrow diffraction peak at around 87° along the (220) direction. From the XRD spectra, it can be obviously seen that all of the Mo films have a sharp (110) peak and this sharpness of the (110) peaks indicates that the Mo films are well crystallized during the deposition. As seen in the Fig. 1 and in Table 2, M1 sample have the most intense (110) peak and the narrowest FWHM degree. In the first series, it was determined by the values of FWHM that the crystallinity of the films decreased by decreasing Ar gas pressure for the M1, M2 and