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Controlled formation of $MoSe_2$ by MoN_x thin film as a diffusion barrier against Se during selenization annealing for CIGS solar cell

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ABSTRACT

This study investigated the interfacial reactions and electrical properties of a Mo single layer and Mo/MoN_x/Mo multilayer during high temperature selenization annealing. The Mo single layer was converted easily to $MoSe_2$, which was 7 times thicker than the Mo layer consumed ~900 nm, by selenization at 460 °C for 10 min and the sheet resistance increased 8 fold compared to that of the as-deposited Mo film. On the other hand, in the Mo/MoN_x/Mo structure, transmission electron microscopy (TEM) showed that the $MoSe_2$ transformation was localized only in the top Mo layer and the bottom Mo layer was completely unaffected, even after selenization at 560 °C. The sheet resistance of the multilayer was relatively unchanged by selenization. This suggests that the MoN_x layer performed well as a diffusion barrier against Se and the thickness of $MoSe_2$ can be controlled precisely by adjusting the top Mo layer thickness. Furthermore, TEM and energy dispersive spectroscopy analysis showed that the selenized multilayer consisted of $MoSe_2$/Mo/MoN_x/Mo, in which the top Mo layer of 60 nm was not fully converted to $MoSe_2$ and 20 nm was left unreacted. The residual Mo interlayer located at the interface of $MoSe_2$ and MoN_x is believed to be beneficial for the ohmic contact of the selenized multilayer.

1. Introduction

Among thin film solar cells reported thus far, Cu(In, Ga)(S, $Se)_2$ (CIGS) solar cells have the highest conversion efficiency at 21.7% [1]. These small-area solar cells feature CIGS absorber layers prepared by a co-evaporation method. Recently, Solar Frontier announced a record conversion efficiency of 20.9% with CIGS produced based on sulfurization after selenization (SAS) [2]. This two-step process, which is comprised of metal precursor deposition followed by chalcogenization, is used widely in the production of large-area modules. Typically, a CIGS absorber layer is formed on top of a Mo back contact. The chalcogenization step of the two-step process involves selenization at relatively low temperatures followed by sulfurization at high temperatures. During the two-step process, the surface of the Mo back contact reacts with Se to form a $MoSe_2$ layer. While Mo selenide facilitates the ohmic contact of CIGS and Mo [3], it can cause a decrease in the fill factor arising from high series resistance [4] or delamination [5] when formed with an excessive thickness. The conversion efficiency increases at higher heat treatment temperatures due to the enhanced structural and electrical quality of CIGS [6], but this entails a trade-off with an excessively thick $MoSe_2$ layer in the case of the two-step process. Therefore, to utilize the benefits of working at high temperatures, it is essential to control the thickness of $MoSe_2$. According to Wada et al., the selenization of Mo is accelerated in the presence of Na [7] because the Se activity increases on the Mo surface in the form of Na polyselenide. Removing Na to suppress $MoSe_2$ growth, however, is not recommended Because Na is essential for creating high-efficiency CIGS solar cells. Another study showed that O in Mo thin films helps suppress the formation of Mo selenide [8]; however, O should not be used to remove $MoSe_2$ because it not only increases Mo resistivity but also suppresses Na diffusion [8].

In this study, the formation of $MoSe_2$ was controlled by introducing a Se diffusion barrier in the middle of the Mo layer. The diffusion barrier must ensure chemical stability with surrounding materials up to the follow-up heat treatment process and prevent the diffusion of some elements. In the manufacture of semiconductor devices, transition metals, such as Ta, Ti, W, and Mo, and their nitrides, such as TaN_x, TiN, WN_x, and MoN_x have been used as diffusion barriers [9,10]. Many investigations on applying such diffusion barriers to Cu show that transition metal nitrides are more effective in preventing diffusion at higher temperatures than transition metals [11–17]. The outstanding diffusion barrier

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performance of transition metal nitrides can be attributed to their excellent thermal stability, dense crystal structure of the interstitial compound, and the stuffing of grain boundaries by nitrogen during sputtering [18,19]. Although the characteristics of MoN_x as a diffusion barrier for Se have not been reported, the MoN_x layer and Mo/MoN_x bilayer are more effective in preventing Cu diffusion than a Mo layer [20]. Therefore, in this study, MoN_x was inserted as a diffusion barrier against Se in the Mo back contact layer to control the thickness of $MoSe_2$ formed during selenization annealing.

Most molybdenum nitride films have been deposited by physical vapor deposition (PVD), e.g., by sputtering [21–26] and ion beam-assisted deposition (IBAD) [27,28]. Chemical vapor deposition (CVD)-based methods are seldom used [29–31] and their use generally results in high resistivity and high levels of impurities within the films. This study deposited MoN_x films through reactive sputtering, which makes it possible to achieve more precise control of the compositions of the compound thin films by adjusting the flow rate of reactive gases and provides easier control of the physical properties. MoN_x forms ohmic contact with Mo and has a low resistivity, allowing the successful application of MoN/Mo to electrodes. Moreover, depending on the presence of reactive gases, processes involving Mo and MoN_x films can be carried out in the same vacuum chamber. This is expected to simplify the process and reduce the cost significantly. This study discussed the effects of MoN_x as a diffusion barrier for Se by analyzing the microstructure of thin-Mo and MoN_x layers after the selenization of a thin-Mo/MoN_x/thick-Mo multilayer at 460–560 °C under a Se vapor atmosphere.

2. Experimental

Mo and MoN_x thin films were deposited by RF (radio-frequency) magnetron sputtering with an N_2/Ar gas mixture. The Mo target used in the deposition process was 5 cm (2 in.) in diameter with a purity of 99.9999%. The flow rate of N_2 gas was varied and the characteristics of the MoN_x thin films were examined accordingly. As a substrate for Mo and MoN_x deposition, soda lime glass or thermally-grown SiO_2 (100 nm) covered Si wafer were used after RCA cleaning. During deposition, the temperature of the substrate and chamber was maintained at 150 °C, and the substrate was rotated at 3 revolutions per minute to allow uniform deposition. For all depositions, the initial vacuum was maintained at below 3.0×10^{-6} torr, and an RF power of 100 W was applied to the target. The flow rate of Ar gas was fixed to 20 sccm (standard cubic centimeter per minute), while that of the N_2 gas was varied from 2, to 14 sccm. The throttle valve was adjusted to maintain a pressure of 8 m torr throughout the deposition process.

Grazing-incidence angle (incident angle, $\theta = 3°$) X-ray diffraction (GIAXRD, PANalytical X'-pert MRD with Cu Kα radiation at 1.2 kW) was performed for phase and crystallinity identification. The resistivity was determined by combining the sheet resistance of the film measured using a four-point probe and the measured thickness. The composition and impurities were identified by Rutherford backscattering spectrometry (RBS). The nitrogen resonance RBS technique (incident energy of He^{++}: 3.695 MeV) was used to detect N in the film.

As shown in Fig. 1, a Mo layer of 650 nm was first deposited on top of the soda lime glass, followed by a 120 nm MoN_x layer, depending on the experimental conditions determined by the N_2 flow rate. A Mo thin film with a thickness of 60 nm was finally deposited. The effectiveness of the diffusion barriers for Se was assessed by comparing the Mo layer (~650 nm) and the Mo/MoN_x/Mo multilayer (total thickness: ~830 nm) after selenization at 460 °C and 560 °C. Selenization was carried out by incorporating Se vapor in the rapid thermal process for ten minutes. The characteristics of the diffusion barriers were evaluated based on interfacial reaction analysis of the bright-field images, scanning TEM-high angle annular dark field (STEM-HAADF) analysis (Hitachi, HF-3300 equipped with 300 kV accelerating voltage and field emission gun) and energy dispersive spectroscopy (EDS). The TEM images were taken digitally using a 2 k × 2 k (2048 pixel × 2048 pixel) charge coupled device (CCD) camera (Gatan UltraScan™ 2000).

3. Results and discussion

Fig. 2 shows the change in resistivity with increasing N_2 flow rate. The Mo thin film deposited using Ar plasma without N_2 had a resistivity of 24 μΩ-cm. When 2 sccm of N_2 gas was flowed into the chamber, the resistivity of the thin film increased to 214 μΩ-cm. Overall, the resistivity of the deposited film increased with increasing N_2 flow rate. When the flow rate of N_2 gas in the chamber was increased to 14 sccm, the resistivity was ~813 μΩ-cm. This is because the electrical resistance increases with the formation of molybdenum nitride from the metal Mo due to the incorporation of N in the thin film at higher N_2 flow rates.

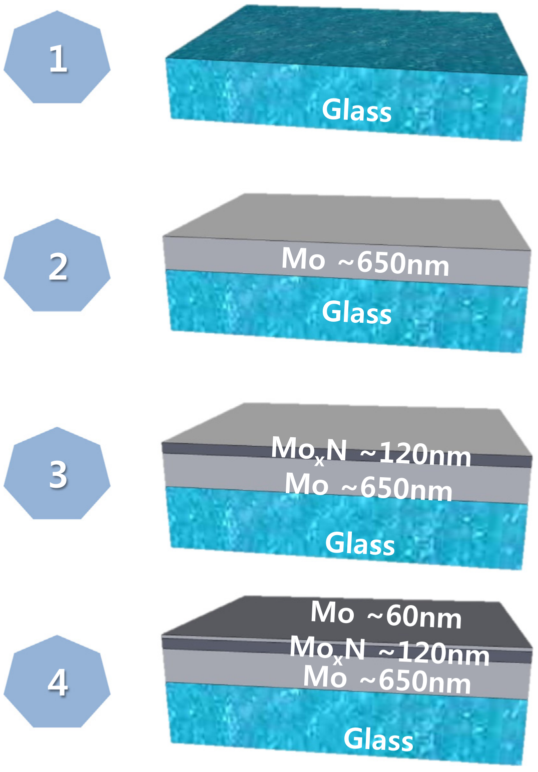

Fig. 1. Schematic diagram of sample structure.

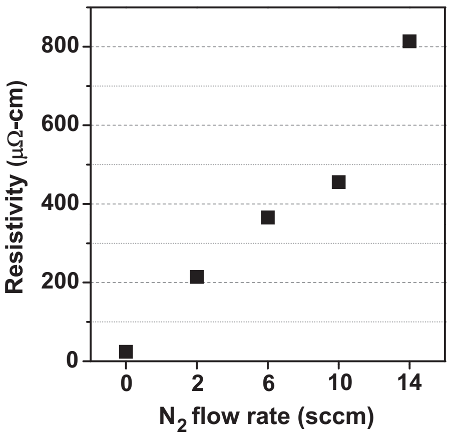

Fig. 2. Resistivity of the films as a function of N_2 flow rate.

Fig. 3 shows the XRD patterns of the deposited films at different N_2 flow rates. Under all deposition conditions, the largest peak was observed at 40.5° 2θ, which was assigned to the (1 1 0) plane of Mo with a body centered cubic (BCC) crystal structure. The (1 1 0) peak of the Mo thin film indicates a crystal structure suitable for growth into the (1 1 2) surface of the CIGS thin films. When the N_2 flow rate was increased to 2 sccm, the XRD pattern of the molybdenum nitrides could not be observed. This suggests that the crystal structure is maintained despite the small amounts of N in Mo. On the