Characterization of TiN back contact interlayers with varied thickness for Cu$_2$ZnSn(S,Se)$_4$ thin film solar cells

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TiN thin films have previously been used as intermediate barrier layers on Mo back contacts in CZTS(e) solar cells to suppress excessive reaction of the Mo in the annealing step. In this work, TiN films with various thickness (20, 50 and 200 nm) were prepared with reactive DC magnetron sputtering on Mo/SLG substrates and annealed, without CZTS(e) layers, in either S or Se atmospheres. The as-deposited references and the annealed samples were characterized with X-ray Photoelectron Spectroscopy, X-ray Diffraction, Time-of-Flight-Elastic Recoil Detection Analysis, Time-of-Flight-Medium-Energy Ion Scattering, Scanning Electron Microscopy and Scanning Transmission Electron Microscopy – Electron Energy Loss Spectroscopy. It was found that the as-deposited TiN layers below 50 nm show discontinuities, which could be related to the surface roughness of the Mo. Upon annealing, TiN layers dramatically reduced the formation of MoS(e)2, but did not prevent the sulfurization or selenization of Mo. The MoS(e)2 had formed near the discontinuities, both below and above the TiN layers. Another unexpected finding was that the thicker TiN layer increased the amount of Na diffused to the surface after anneal, and we suggest that this effect is related to the Na affinity of the TiN layers and the MoS(e)2 thickness.© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

By 2050 the International Energy Agency anticipates that solar power will become our largest source of electricity with photovoltaics PV contributing to 16% of the total electricity production [1], up from today's 1.8% [2]. The volumes required will have a major impact on PV technologies in terms of resources. This is why Cu$_2$ZnSn(S,Se)$_4$ (CZTS(e)) thin film solar cells have gained attention during recent years due to their composition of non-toxic and earth abundant materials. The development of CZTS has, however, encountered major challenges that need to be solved. The back contact (BC) and the interface between the BC and the CZTS(e) absorber layer has been identified as one of these major challenges [3]. The challenges are mainly related to the control of interfacial reactions, minimizing series resistance and decreasing optical losses [4], but also the more practical issue of delamination (“peeling”) of the absorber layer from the BC. Exploiting an alternative back contact to the dominating Mo that could overcome the issues mentioned above could be beneficial for the solar cell performance itself, but has also potential to increase the process window in particular for annealing. Mo has for long time been the main material of choice for BCs in both CIGS(e) and CTZS(e) and has been extensively studied (see e.g. [5–11]). Several other materials have been investigated as alternative BCs, such as W, Cr, Ta, Nb, V and Mn [12]. However, the interface between the Mo and CZTS(e) has been shown to be unstable at typical anneal temperatures [13], and a thick layer of MoS(e)2 is often present after annealing. The MoS(e)2 has the benefit of creating a good ohmic contact, but could also cause series resistance. Furthermore, the MoS(e)2 layer is a source of the adhesion problems, partly due to its layered structure, in fact, MoS$_2$ is a well-known industrial solid lubricant [14]. For these reasons, several studies on different interlayer materials for CZTS(e) have been published, including Au, Pt, Pd, W, Ni [15], TiN, TiW, Cr, Ti, Al [16], Ag [17,18], TiB$_2$ [19], C [20], ZnO [21,22], Bi [23], MoO$_3$ [24], MoO$_2$ [25] with several candidates showing promising results and improvements compared to references using Mo BC. TiN has good electrical properties: the work function is close to that of Mo and could be considered as an ohmic contact [16] and it has better reflectance compared to Mo, especially for long wavelengths [26]. In several studies where TiN as an intermediate layer on top of a Mo BC has been investigated, the solar cells have shown superior performance compared to the bare Mo BC references, as in the cases of Shin et al. [27], Oueslati et al. [16] and Schnabel et al. [28]. Scragg et al. got solar cell enhancement and adhesion improvement by using TiN interlayer between CZTS and Mo BC under some annealing conditions [29]. Nevertheless, there are also publications that report no improvement for solar cells when using TiN as interlayer (e.g. [25]). Although it is likely that

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the properties of the interlayer may have a great influence on the results, a common problem in the previous studies is the lack of experimental details and understanding of the TiN barrier layer itself, which makes it difficult to understand the reasons for the scattered results in literature. In this study, we decided to make an in-depth characterization of the TiN layers on top of the Mo/SLG substrate, in a model experiment without additional CZTS(e) layers, before and after typical annealing process. We further investigated on the functionality of the TiN interlayer, which includes its barrier properties (blocking/diffusion of S(e), formation of MoS(e)2 and Na diffusion) and the effect of the thickness of TiN layer. In previous studies on annealed samples with TiN-coated Mo substrates, MoS(e)2 has been nearly eliminated by thin layers of TiN but still present in detectable amounts. One aim of this study is to investigate the MoS(e)2 in detail and whether the formation can be completely suppressed by introducing thicker layers than have been tried before. The presence of Na in the absorber layer has previously been extensively investigated and consensus is established that the amount of Na in the absorber layer has a significant effect on device performance. Earlier studies on interlayers have not focused on Na diffusion, if mentioned at all. The assumption that interlayers might have a negative effect on the Na diffusion is common [e.g. as in [30]], although a few studies indicate that this is not the case [e.g. [16,29]]. Another aim of this study is therefore to investigate the effect of thickness of TiN interlayers on Na diffusion.

2. Experimental details

Mo was deposited on SLG substrate by DC magnetron sputtering in an in-line sputtering system from Material Research Corporation using Ar (purity 99.9995%, supplied by Air Liquide) as sputtering gas and a planar Mo target (99.97%, Plansee) with dimensions 120 mm × 378 mm. The Mo films have bilayer stack. It was made by first sputtering a highly adhesive layer at 2 Pa and 2000 W (4.4 W/cm2) and then a highly conductive layer at 0.8 Pa and 2000 W. The total bilayer Mo thickness was approximately 350 nm. TiN layers were reactively sputtered in a von Ardenne CS 730 S sputtering system using DC magnetron sputtering from a 152 mm circular Ti target (99.9995%, FHR Centrotchem Group) in Ar (99.9995%, Air Liquide) and N2 (99.9999%, Air Liquide) atmosphere. The background pressure was 10−5 Pa and total pressure during sputtering was 0.8 Pa with Ar flow set to 20 sccm and N2 to 45 sccm (N2/Ar = 2.25), power of 1000 W (4.3 W/cm2) and current of 2.2 A. The deposition rate was 1.64 nm/s. TiN layers with thicknesses of 20, 50 and 200 nm were prepared. The thicknesses were validated with profilometer (Veeco Instrument, Dektak 150). These settings should according to [31,32] produce stoichiometric TiN layers with relatively low resistivity and good thermal and morphological stability.

The TiN/Mo/SLG samples were then annealed in a pyrolytic carbon (PyC) coated graphite box with a volume of 15 cm3 inserted in a preheated tube furnace with a central hot zone and an outer water-cooled zone/loading area. Fast heating and cooling were achieved by transferring the sample box from the cold zone into the hot furnace using a rod. Two separate annealing experiments were performed, one in S atmosphere and one in Se atmosphere, with four samples with the size of 25 mm × 25 mm in each annealing. The thickness of the TiN layer (0, 20, 50 and 200 nm) is the only variable in each annealing batch. For the annealing in sulfur excess environment, the temperature in the hot zone was 585 °C, the background Ar pressure was set to 47 kPa and the annealing dwell time was 13 min, with 80 mg of solid S placed in the PyC coated graphite box. For the annealing in selenium excess environment, the temperature in the hot zone was 585 °C at 35 kPa and the annealing dwell time was 4 min, with 85 mg of solid Se placed in the box. Different boxes were used for the different anneals to minimize cross-contamination and the furnace was cleaned between the anneals. The process parameters were mainly chosen based on the baseline process for annealing of CZTS as described in [33]. An identical set of reference samples was kept unannealed.

The surface of all samples was analyzed by x-ray photoelectron spectroscopy (XPS), with a depth information of about few nanometer. The system was a PHI Quantum 2000 Scanning ESCA microprobe from Physical Electronics, using monochromatic Al Kα radiation (1486.7 eV), and the measured spot size on the sample was 200 μm. The resulting spectra were analyzed with the software Multipak and CasaXPS.

Crystallographic properties were analyzed by x-ray diffraction (XRD), both in θ-2θ-mode (contribution from ordered orientation) and grazing incidence (GIXRD, contribution from random orientation) in Siemens D5000 systems and evaluated and the phase identification was done by comparing to database patterns in the software highscore+.

The morphology of the samples were analyzed by scanning electron microscopy (SEM) in a Zeiss 1550 system with a high resolution Schottky FEG and an inlens detector. Sample composition profiles were obtained by time-of-flight-energy elastic recoil detection analysis (ToF-E ERDA using the Tandem accelerator at Uppsala University. 135 ions with 36 MeV primary energy were impinging for 67.5° incoming angle and recoiling particles were detected at 67.5° exit angle by two carbon foil ToF detectors and Si surface barrier detector for energy discrimination. The acquired data was converted to depth profiles using the software Conversion of Time-Energy Spectra (CONTES) [34].

Near surface composition was measured with Time-of-Flight-Medium-Energy Ion Scattering (ToF-MEIS, the system is described in detail by Linnardsson et al. [35]). He+ ions were accelerated to 80 keV and scattered ions detected with a large solid angle MCP-detector at 15° scattering angle. MEIS simulations were performed in SIMNRA [36].

Transmission Electron Microscopy (TEM) lamellae of the 20 nm TiN reference, and 20 nm TiN selenized sample were prepared using a Focused Ion Beam (FIB) (FEI Strata DB235 FIB-SEM), following the in-situ lift-out method [37]. The Scanning Transmission Electron Microscopy (STEM) and the Electron Energy Loss Spectroscopy (EELS) analyses were realized in a FEI Tecnai F30 ST at 300 keV equipped with a Tridimen filter. Chemical composition maps were treated by a Multivariate Statistical Analysis tool to improve the signal to noise ratio [38].

3. Results and discussion

The samples were first visually assessed after the annealing and compared to the unaannealed reference samples. The sulfurized samples had a very slight color change after the annealing but no other visible effects such as flaking or peeling. The selenized samples on the other hand had a more discernible color change after the annealing and small areas where flaking had occurred. The most severe flaking had occurred on the sample without the TiN layer, and then the flaking was reduced with the increasing thickness of TiN. The flaked areas were visible from the backside of the glass, i.e. the Se had reacted through the stack. In all the following analyses, areas without flaking features were chosen for examination.

The Mo 3d peaks from the reference-, sulfurred and selenized samples are shown in Fig. 1(a–c). The Mo 3d peaks in Fig. 1(a) for the bare Mo sample consists of several doublets fitting well to the Mo 3d–energies of Mo, MoO2 and MoO3 [39]. Moreover, the O 1s peak (not shown here) is also broadened towards the higher binding energy side, indicating several bondings states corresponding to O in MoO2 and MoO3. The presence of oxygen could be important to notice as it was previously shown that the O content in the Mo affects the diffusion of Na [40]. In Fig. 1(a) the Mo 3d doublet peak appears also for the 20 nm TiN reference sample, indicating that the Mo is exposed to the surface. Noticeable is also that the binding energy of the Mo 3d doublet from the 20 nm TiN sample is in agreement with the tabulated value of MoO3 (and not e.g. MoN, as it would appear around 228.5 eV according to [41]), indicating that the Mo at Mo/TiN interface is heavily oxidized and only appears in

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the oxidized state. The Mo 3d peaks of the sulfurized and the selenized samples (shown in Fig. 1b and c) are significantly different from the reference samples, and the Mo 3d peaks appear both for the bare Mo, the 20 nm and the 50 nm TiN samples, indicating that the amount of Mo at the surface increased during the annealing. After annealing the Mo 3d peaks are shifted to higher binding energies that resembles MoS2 and MoSe2 (see e.g. [42], for Mo 3d for MoSe2) respectively. The main peaks of S 2p and Se 3d (not shown here) follow the trend of the Mo 3d peaks, i.e. decreasing intensity with increasing TiN layer thickness. Corresponding peaks of S 2s and Se 3s are seen in Fig. 1(b) and (c), which follow the same trend. The S 2p peaks do also have small peaks at the binding energy expected for Na2SO4 (168.8 eV) and it follows which follow the same trend. The S 2p peaks do also have small peaks that could be related to the heat-up of the Mo during TiN-sputtering, and give similar effect as the pre-annealed Mo, as described in e.g. [43,44,45]. It could also be related to the thickness of the MoS(e)2-layer (which in turn may be related to the thickness of the TiN-layer) or the change in interface chemistry (e.g. O content).

The Ti 2p peaks (not shown here) have the shape of twin doublet peaks that fit with the overlapping peaks of TiN and TiOx. To completely resolve TiOx from TiN in XPS is difficult since there could also be intermediate compound of Ti–N–O at the surface of the TiN [46]. The formation of TiOx on the TiN surface is not unexpected for the as sputtered TiN at room temperature. Observation of TiOx on the air exposed sputtered TiN film surface has been reported before [46] and this agrees well with our results here. Furthermore, the oxidation of the TiN surface becomes more apparent for the samples annealed in sulfur, where the main Ti 2p peak shifts towards oxide rich side from 457.9 to 458.6 eV (not shown here).

Diffraction patterns were obtained from all samples both with Θ–2Θ XRD and GIXRD (not shown here). TiN films are mainly oriented in [111] and not in [200] as expected for the chosen parameters [32], likely because of different substrates were used. Both the sulfurized and the selenized bare Mo samples have MoS(e)2 peaks both in Θ–2Θ and GIXRD, which shows that they all had MoS(e)2 with crystal orientations in terms of c-axis both perpendicular and parallel to the surface, of which the latter potentially could suppress diffusion of Na [46]. For the samples with TiN the MoS(e)2 peaks were greatly reduced similar to previous reports, e.g. [27,29]. MoS(e)2 peaks were present in all annealed samples with 20 and 50 nm TiN, but could not be concluded for the samples with 200 nm TiN.

In the SEM, MoS(e)2 layers were seen on the annealed samples without TiN, as shown in Fig. 2(a) and (c). The MoS(e)2 was reduced to unresolvable thickness for all samples with TiN (e.g. as in Fig. 2(d)) and its presence in the 200 nm TiN samples could not be confirmed by SEM. The top view SEM of the unannealed reference sample with 20 nm TiN (Fig. 2(d)) shows a discernible contrast between the lighter Mo grain peaks and the darker valleys at the grain boundaries. These darker spots could match with discontinuities in the thin TiN film caused by insufficient step coverage of the TiN sputtering. This contrast is greatly reduced for the unannealed sample with 50 and 200 nm TiN (not shown here).
here). This would explain the presence and absence of Mo peaks in the XPS measurement for the respective samples. The morphology clearly changes after the annealing, as the grains visible in the top view images in Fig. 2(e) and (f) are blunt compared to those in (d). The blurry areas in (e) and the bright areas seen in (f) could be MoSe₂ (seen in XPS).

ToF-ERDA was measured in order to obtain depth profiles of the composition and confirm whether MoS₂ was present below the TiN layers in the annealed samples for all thicknesses or not. The composition of the bulk of the as-deposited TiN layers (200 nm) was confirmed by ToF-ERDA to be stoichiometric TiN within the accuracy of the method (~1%). The ToF-ERDA depth profiles of the reference samples, seen in Fig. 3(a) and (d) correlate well with the XPS spectra regarding the observation of Mo exposed to the surface before annealing. As seen in Fig. 3(a) the Mo depth profile of the 20 nm TiN reference extends all the way to the surface, while it for the 200 nm sample, seen in Fig. 3(d), it clearly does not extend to the surface. For the 50 nm
sample (not shown here) the profile was close to reach the surface. However, it is clearly seen for all thicknesses, both for the sulfurized samples (Fig. 3(b) and (d)) and the selenized samples (not shown here) that there is S(e) present below the TiN layer for all samples. This shows that the TiN layers in principle is not blocking the S(e) even when 200 nm TiN is used. The concentrations of Na are too low to be accurately analyzed in the depth profiles, but Na recoil tracks are clearly visible in Fig. 3(c) and (f). An accumulation of Na correlates with the TiN-layer, indicating that the TiN layer in fact acts as a sink for Na. An accumulation of Na close to the surface is however seen also for the sulfurized/selenized samples without TiN (not shown here), but its recoil tracks extends through the whole Mo layer and do not have the same pattern as the samples with TiN have. The depth profiles show that all interfaces, i.e. the surface and the TiN/Mo interface, have increased O content compared to the bulk. We can also see here, just as in the XPS, that the oxygen content of the TiN surfaces has increased after anneal.

ToF-MEIS was measured with the intention to get highly resolved information about the surface geometry. In particular regarding the observations in XPS; the surface-exposed Mo on the unannealed 20 nm reference sample, and the increased amount of Mo at the surface of the samples with 20 (and 50) nm TiN after annealing. MEIS has a beam spot size of around 1 mm², so the size of the measured area exceeds the areas of the other measurements by orders of magnitudes. The 20 nm samples were measured and the spectra can be seen in Fig. 4 together with simulations of a continuous TiN-layer (red line) and two discontinuous TiN layers (black lines) with varied coverage. We can see that the unannealed sample to large extent resembles the simulation with 90% TiN coverage, but Na recoil tracks are not covered with TiN. It also consistent with and explains the Mo visible at the surface in the XPS (Fig. 1(a)), as well as the MEIS results. The images of the selenized sample in Fig. 5(b, Mo map) and (c, Se map) show the presence of Mo above the discontinuities of the TiN layer, and Se both above and below the TiN layer. For the same spots were Se is present in the Se map, we see a weakened signal below the layer in the Mo map. This strongly indicates the presence of MoSe2 in the area near the discontinuities of the TiN layer, and it is likely that this is what we see in the top view SEM in Fig. 2(e). This is also consistent with the results from XPS and MEIS, so we can rule out that this would be an artefact from the lamellae preparation in the FIB. It once again confirms that Mo accumulates at the surface in the state of MoS(e)2 during anneal. The observation could possibly explain the flaking of the TiN layer during the selenization. We could see in Fig. 2 that the volume expansion is significant when MoSe2 forms. This volume expansion, which is located below the openings in the TiN layer could potentially break the layer. Consequently, the flaking of the TiN barrier would expose bare metallic Mo which would react with Se through the whole Mo layer. The STEM images could also give a possible explanation to the Na diffusion behavior seen in the XPS, which is, the thicker TiN (and less MoS(e)2, as observed in XPS), the more Na. The MoS(e)2 forms around the openings in the TiN layer and could then act as plugs in the TiN discontinuities and consequently inhibit the Na diffusion. Thicker TiN layers could possibly reduce the MoS(e)2 formation and thus increase the diffusion of Na to the surface.

Fig. 4. ToF-MEIS spectra of 20 nm TiN samples analyzed with 80 keV He⁺ ions. Thinner lines shows simulations of a continuous 20 nm TiN layer, and two discontinuous 20 nm TiN layer with 90% and 99% coverage respectively. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
Tin layers with various thicknesses (20, 50 and 200 nm) were deposited on Mo and annealed either in S or Se atmosphere. The TiN layers were inert except for some oxidation near the surface after anneal. Due to non-uniform coverage related to the surface roughness of Mo, they did not completely inhibit S(e) from reacting with the Mo. MoS(e)2 was present near the discontinuities of the TiN layers. The TiN layer did also not block Na diffusion, on the contrary, a thicker TiN layer increased the amount of Na at the surface after annealing. Several observations were made that possibly could explain this phenomenon. Na was observed to accumulate in the TiN layer, which could act as a sink for Na. Na diffusion could possibly also be related to the thickness of MoS(e)2, which we expect to be inversely related to the thickness of TiN layer. Thicker MoS(e)2 is expected to block the Na transport. In the nearest future, studies should include device making with the same BC stack as used in this paper. However, more work needs to be focused on the effects of BC properties have on device performance and properties. As shown in this work, there are unexpected effects related to the interlayer on the BC. A deeper understanding of these effects has potential to open up pathways for better control of interfacial chemistry.

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