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EFFECT OF Na INCORPORATION ON THE GROWTH AND PROPERTIES OF CdTe/CdS DEVICES

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ABSTRACT

Sodium is known to enhance p-type doping in copper indium diselenide (CIS)-based devices fabricated on soda-lime glass substrates, and similar amounts of Na are present in commercial cadmium telluride (CdTe) devices. We present the results on the effects of Na incorporation on the properties of CdTe/CdS solar cells prepared on borosilicate glass substrates. A NaF layer 10 to 30 nm thick was incorporated at either the CdS/CdTe interface or on the CdTe surface, as a source of Na. CdTe layers were deposited by close-spaced sublimation at substrate temperatures from 425°C (LT) to 620°C (HT), followed by heat-treatment in the presence of $CdCl_2$ vapor. Atomic force microscopy analysis showed that the samples with NaF at the CdS/CdTe interface deposited in He ambient have larger grains with a sub-grain structure that disappears after $CdCl_2$ heat treatment accompanied by an increase in grain size. Samples deposited in O_2 ambient have smaller grains without a sub-grain structure. For samples with NaF deposited on the CdTe surface, LT samples with $CdCl_2$ heat treatment showed a morphology similar to samples without NaF layers; but samples heat-treated in He ambient at 500°C prior to $CdCl_2$ treatment showed a different microstructure with platelets on the surface. HT samples with a NaF layer at the CdTe surface showed an additional layer at the surface with both types of heat treatments, indicating that NaF does not react readily for these samples. In addition to the discussion of the effect of Na incorporation on the material properties, we will include preliminary data on the effect of Na incorporation at the interface or surface on device properties.

INTRODUCTION

Best device performance for CdTe solar cells have been achieved for devices fabricated on borosilicate 7059 glass substrates [1]. These substrates differ from soda-lime glass substrates used in the industry in two main aspects, namely, the difference in thermal coefficient of expansion (TCE) and the Na in soda-lime glass. The TCE of borosilicate glass is comparable to that of CdTe, whereas the TCE of soda-lime glass substrates is nearly twice that of CdTe. In addition, a significant amount of Na is found in the cells fabricated on soda-lime glass substrates. Both of these factors are considered to be responsible for inferior performance of the devices fabricated on soda-lime glass substrates. In the case of CIS- based devices, the situation is exactly opposite and record-efficiency devices have been obtained only on soda-lime glass substrates. Improved the device performance is attributed to the enhancement of p-type doping in CIGS absorber material and grain growth. In the case of CdTe-based devices, there is limited knowledge on the influence of Na on the material and device properties [1]. Because considerable amounts of Na are present in the devices prepared on the soda-lime substrates used by the industries, it is necessary to determine its effect on device properties. In addition, the open-circuit voltage (V_{oc}) of CdS/CdTe thin-film solar cells is limited to 850 mV, and it is desirable to explore ways of increasing it. To first order, the V_{oc} is directly proportional to the carrier concentration in the CdTe absorber. It is well known that it is difficult to achieve appreciable p-type conductivity in CdTe because of the self-compensation and low solubility of dopants. Substitution of Group V impurities (As, P, Sb) on the anion site has been studied in detail [2]. Group IB (Cu, Ag) impurities introduce deep levels and are unsuitable for achieving an increase in conductivity. One avenue that has not been explored in sufficient detail is the doping of CdTe by Group IA impurities (Li, Na). Interestingly, the ionization energy of acceptor levels introduced by Li and Na doping are reported to be about 58 meV, and this value is very close to the effective mass limit [3]. Hence, there is ample justification for performing a controlled experimental study of p-type doping of CdTe with Na impurities. Deliberate incorporation of Na in $CuInSe_2$ alloys has led to remarkable improvements in device properties [4]. $CuInSe_2$ is a derivative of the binary II-VI family, and the defect physics is expected to translate readily.

In this work, we have incorporated thin layers of NaF (10–30 nm) at the interface region of the CdS/CdTe structures. NaF was deposited by electron-beam evaporation onto CdS surfaces prepared by chemical-bath deposition (CBD) onto tin oxide-coated glass substrates. The NaF layer is expected to decompose at high substrate temperature and release the Na and F. For low substrate temperatures, the layer may remain intact. The presence of a thin, foreign layer alone can influence the growth habit of CdTe.

EXPERIMENTAL

Corning borosilicate 7059 glass coated with F-doped SnO_2 with sheet resistivity of 8 ohms/sq and 80-nm CdS deposited by CBD were used as the substrates in this study. NaF layers with thicknesses in the range of 10–30

nm were deposited at room temperature by vacuum evaporation. CdTe layers were deposited by close-spaced sublimation (CSS) at substrate temperatures of 425°C (LT) and 620°C (HT), with thicknesses in the range of 6–8 μm. Two types of structures were fabricated for this study: glass/SnO$_2$/CdS/NaF/CdTe—to study the effect of Na at the interface, and glass/SnO$_2$/CdS/CdTe/NaF—to examine the influence on the properties of CdTe. Two types of heat treatments were used in this study: post-deposition heat-treatment was performed in He ambient and/or in the presence of CdCl$_2$ vapor. Cu-doped graphite paste was used to make contact to CdTe. Morphology of the samples was analyzed by atomic force microscopy (AFM).

RESULTS AND DISCUSSION

AFM analysis was used to study the effect of a NaF layer at the CdS/CdTe interface and the deposition conditions on the microstructure of CdTe films. The LT sample with NaF at the CdS/CdTe interface showed a significantly different microstructure as compared to the samples without the presence of Na. Figure 1a shows the AFM image of an as-deposited LT CdTe sample deposited on glass/SnO$_2$/CdS/NaF substrate in He ambient. These films exhibit larger grains compared to the films deposited directly on CdS under identical conditions. Films on NaF substrate are also more compact and show a sub-grain structure not observed in the films on CdS.
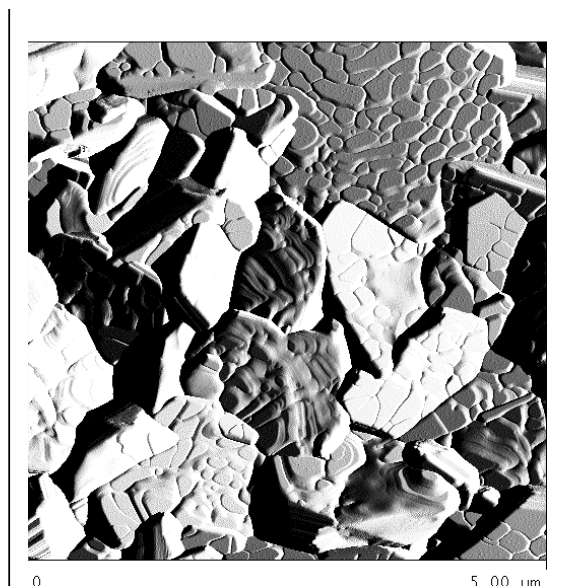

Fig. 1a. AFM image of as-deposited LT sample deposited on glass/SnO$_2$/CdS/NaF in He ambient.

Fig. 1b. AFM image of CdCl$_2$-treated LT CdTe sample deposited on glass/SnO$_2$/CdS/NaF in He ambient.

Figure 1b shows the AFM image of a LT CdTe sample deposited on glass/SnO$_2$/CdS/NaF substrate in He ambient and CdCl$_2$-treated at 425°C for 5 min. The sub-grain structure disappears after CdCl$_2$ heat treatment, and there is an increase in grain size similar to CdCl$_2$-treated films deposited on CdS. The grain size of the LT sample deposited on a substrate without NaF layer, i.e., directly on CdS, is around 0.5 μm and increases to 2 μm after CdCl$_2$ heat treatment, which is almost comparable to the as-deposited LT sample deposited on NaF.

The presence of O$_2$ in the deposition ambient during CSS deposition of CdTe has a significant effect on the grain size, as well as on the microstructure of the films. As-deposited LT samples deposited in a He/O$_2$ ambient with NaF at the CdS/CdTe interface have smaller grains as compared to samples deposited in an O$_2$-free ambient (Fig. 1a), but do not show any sub-grain structure. Figure 2a shows the morphology of an as-deposited LT CdTe sample deposited on glass/SnO$_2$/CdS/NaF surface in a He/O$_2$ ambient.

Fig. 2b. AFM image of CdCl$_2$-treated LT CdTe sample deposited on glass/SnO$_2$/CdS/NaF in He/O$_2$ ambient.

This sample showed morphology similar to the LT CdTe samples deposited directly on CdS. In these samples, the presence of a NaF layer mainly influences the grain size of the CdTe layer. Figure 2b is an AFM micrograph of CdCl$_2$-treated LT sample deposited on glass/SnO$_2$/CdS/NaF surface in a He/O$_2$ ambient. There is an increase in the grain size of this sample, and it also shows a loss of faceting seen in the as-deposited sample (Fig. 2a). Again
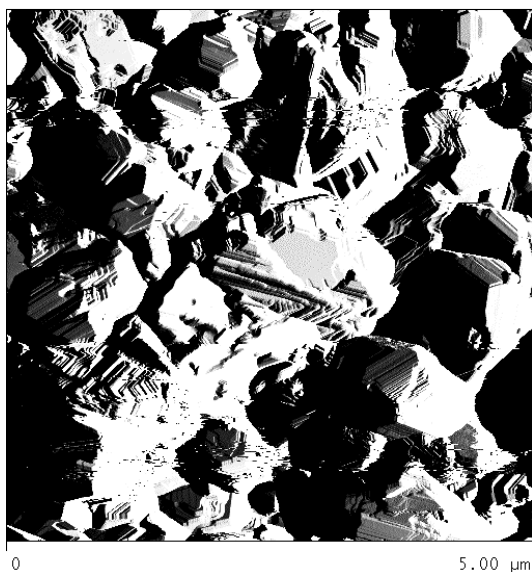

Fig. 2a. AFM image of as-deposited LT CdTe sample deposited on glass/SnO$_2$/CdS/NaF in He/O$_2$ ambient.

these results are similar to samples deposited directly on CdS films.

In the second set of experiments, we looked at the microstructure of samples with a NaF layer deposited on the CdTe surface after two types of heat treatments. Figure 3a shows an AFM image of a HT CdTe sample with a 30-nm-thick NaF layer after a 400°C CdCl$_2$ heat treatment. The image is similar to the one for a sample before the treatment. In both cases, we see the NaF layer on the surface. Pre-heat-treatment in He at 500°C before CdCl$_2$ heat treatment also did not have any effect on the microstructure.

Figure 3b shows an AFM image of a LT CdTe sample with a 30-nm-thick NaF layer after 425°C CdCl$_2$ HT. This sample shows significant change in grain size, as well as in microstructure. A similar sample with a pre- heat-treatment in He at 500°C before CdCl$_2$ heat treatment shows a different microstructure, as well as platelets on the surface. It appears that the heat treatment in He, even at 500°C, induces recrystallization in LT samples with the NaF layer.

In summary, our microstructural investigation shows that the effect of a NaF layer at the CdS/CdTe interface is significant for the CdTe samples deposited at lower substrate temperatures, particularly in an O$_2$-free ambient. The grain size of the samples is considerably larger than for films deposited directly on CdS films.

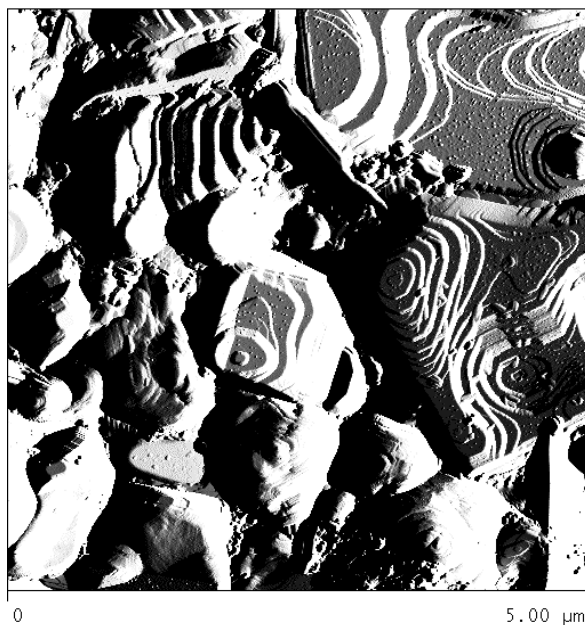Fig. 3b. AFM image of LT CdTe sample with a 30-nm-thick NaF layer after 425°C CdCl$_2$ heat treatment.
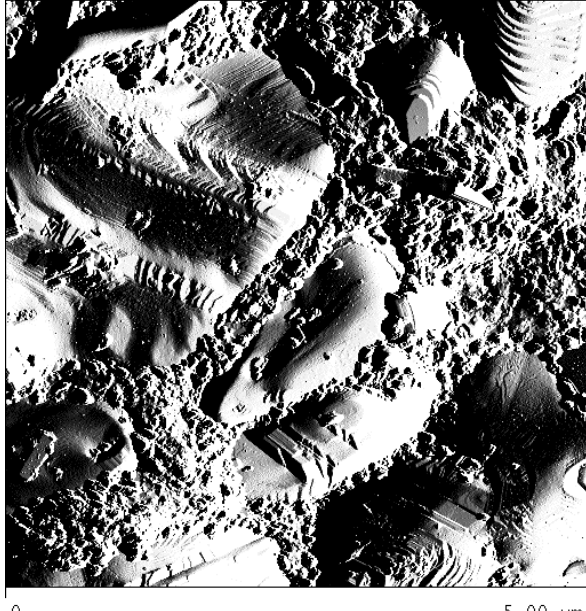
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Fig. 3a. AFM image of HT CdTe sample with a 30-nm-thick NaF layer after 400°C CdCl$_2$ heat treatment.

Devices were fabricated using these samples with CuTe-doped graphite paste. The samples were etched in NPH or Br/methanol prior to application of the paste. Baseline devices (deposited at 620°C, with 400°C/5 min CdCl$_2$ anneal) were also fabricated in the same batch to serve as a reference. The baseline device had a V_{oc} = 809 mV, short-circuit current density (J_{sc}) = 21.3 mA/cm^2, fill factor (FF) = 66.8%, and efficiency of 11.5%.

The devices fabricated from as-deposited LT samples in an O$_2$-free ambient with NaF at the interface showed had a reasonable V_{oc} of 660 mV, but suffered mainly from low J_{sc} (7 mA/cm^2) and low FF (27%). A similar sample using CdTe deposited in an O$_2$ ambient had some improvement in J_{sc} (11 mA/cm^2) and FF (37%). It is noteworthy that although the device performance of these devices is poor, devices prepared from similar samples deposited on CdS show negligible photoactivity. Improvement in the device performance is possibly related to the increased grain size of samples deposited on NaF substrates. CdCl$_2$ heat treatment did not improve the device performance for these devices.

The devices prepared from samples deposited in an O$_2$ ambient on a NaF layer at 500°C gave a V_{oc} of 630 mV, J_{sc} of 15.2 mA/cm^2, and FF of 42%. A similar sample deposited in an O$_2$ ambient had a V_{oc} of 695 mV, J_{sc} of 19.5 mA/cm^2, and FF of 44%.

A possible explanation for the inferior performance of LT CdTe devices with NaF at the CdS/CdTe interface may be the relative stability of the NaF layer at 425°C. Such a high-resistivity layer at the junction would deteriorate the FF of the devices. With an increase in the substrate temperature to 500°C, there is an improvement in all device parameters, possibly due to a partial decomposition of the NaF layer at the interface. Devices deposited at both temperatures show a beneficial effect of O$_2$ on the device performance.

Finally, the devices fabricated using samples with a NaF layer at the back contact showed interesting results. For HT samples in this set, the samples with a Br/methanol etch had lowered device parameters; but the performance of devices with a NPH etch was comparable to the baseline devices. These results are due to the difference in the etching action of the two types of etches. From the AFM image of Fig. 3a, we know that the NaF layer remains intact after a 500°C heat treatment in He, as well as in the CdCl$_2$ heat treatment. The Br/methanol etch removes a very thin layer from the sample, and thus leaves the high-resistivity NaF layer intact at the back contact, thereby affecting the device parameters. On the other hand, NPH etch attacks the top 100 nm of the sample, thus creating a conducting Te-rich region and possibly eliminating the remaining NaF layer from the back surface. This situation can explain the improved performance of NPH-treated devices. In the case of devices prepared from LT samples in this set, performance of devices prepared using both types showed poor performance. Microstructural analysis of these samples (Fig. 3b) showed recrystallization for both. During the process, the NaF layer may have been mixed with the bulk of CdTe. Thus, removal of the top layer with the NPH etch did not eliminate the NaF layer, as in the case of HT samples.

CONCLUSIONS

A NaF layer at the CdS/CdTe interface is helpful for improving the structural quality of CdTe layers. The CdTe films show grain growth, are compact, and the grain size of the films is significantly larger than the films deposited directly on the CdS surface. The effect of the inclusion of a NaF layer at the interface is more pronounced for the CdTe films grown in an O$_2$-free ambient. In the case of glass/SnO$_2$/CdS/CdTe/NaF samples with NaF deposited on CdTe, HT samples showed that CdCl$_2$ and He heat treatments did not produce any structural changes and the NaF layer remained intact. On the other hand, LT samples with NaF deposited on CdTe showed significant structural changes with change in morphology and grain growth during heat treatments, resulting in the inclusion of a NaF layer in the bulk of CdTe during the process.

In summary, we have shown that the inclusion of a thin NaF layer results in an increase in grain size of CdTe deposited at low temperatures. This effect might be helpful in recrystallizing the interface region. Electronic effects of Na may be realized fully when NaF dissociates and the Na atoms are allowed to diffuse.

Devices with a NaF layer at the CdS/CdTe interface gave poor results for the LT samples deposited at 425°C, because NaF did not dissociate at this temperature. The device performance improved for the samples deposited at 500°C, which may be due to partial decomposition of the NaF layer at 500°C, thus reducing the effect of the high-resistivity NaF layer at the interface. We will work on the devices fabricated at higher substrate temperatures, where a complete decomposition of NaF will be possible, thus eliminating the effect of the high-resistivity NaF layer on the device properties.

ACKNOWLEDGEMENTS

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