HIGH EFFICIENCY CdTe/CdS THIN FILM SOLAR CELLS WITH A NOVEL BACK-CONTACT

Nicola Romeo^a, Alessio Bosio^a, Samantha Mazzamuto^a, Alessandro Romeo^b, Lidice Vaillant-Roca^c

^a University of Parma, INFM- Physics Department, V.le G.P.Usberti, 7A-43100 Parma, Italy,
^b University of Verona, Physics Department, Cà Vignal 2-Strada delle Grazie-37134, Verona, Italy,
^c Facultad de Fisica-IMRE, Universidad de La Habana, 43100, La Habana, Cuba.

ABSTRACT: The back contact is probably the most critical step in the fabrication of high efficiency CdTe/CdS thin film solar cells. Usually, it is done first by etching the CdTe surface in order to form a Te rich surface and second by depositing a small amount of Cu, on the order of 2nm, on top of etched CdTe surface. In this way a Cu_xTe layer forms that seems to behave as a non rectifying contact for CdTe. If more copper is used, there is the risk that Cu in excess diffuses into the CdTe/CdS structure causing shunt paths by segregating into the grain boundaries or lowering the cell efficiency by doping CdS thus increasing its resistivity.

In this paper, we propose a novel approach to avoid the Cu diffusion. First of all we do not etch the CdTe surface, second we deposit on top of a not etched surface 100-200nm of a buffer layer, that is As_2Te_3 , followed by the deposition of 10-20nm of Cu. If the deposition of Cu is done at 150-200°C substrate temperature, a reaction between Cu and As_2Te_3 happens that forms a Cu_xTe layer by a substitution reaction. This type of contact resulted to be stable and non rectifying.

Stable solar cells with efficiency close to 16% have been fabricated with this contact. Keywords: Back Contact, CdTe, Thin Film

1 INTRODUCTION

The back contact in the CdTe/CdS thin film solar cell is a very important part of the device fabrication. A not ohmic contact causes a "roll-over" in the I-V characteristic that lowers the fill factor and, as a consequence, the cell efficiency [1]. Since CdTe exhibits a high electronic affinity (χ), most metals form a Schottky barrier that limits the hole transport in the p-type CdTe. The most commonly used metal to make a not rectifying contact with CdTe is Copper. However, before Cu deposition, a chemical etch of CdTe is needed in order to create a Te-rich surface that, reacting with Cu, forms the compound $Cu_x Te (1 \le x \le 2)$ [2-5]. The ohmic contact is not done directly with Cu, that easily diffuses into the CdTe matrix, but with the CuxTe compound that is formed on the CdTe surface [6]. Cu_xTe with x > 1.4 is not a stable material [7] and, as a consequence, it frees copper that, being a fast diffuser, penetrates into the CdTe matrix causing two drawbacks: 1) it segregates into the grain boundaries forming shunting paths and 2) it arrives into CdTe/CdS interface and forms a deep level in CdS that captures electrons increasing the CdS resistivity. Since Cu is a positive ion, its diffusion inside the CdTe/CdS structure depends on the junction internal field that, in turn, depends on the fact that the cell is driven by an external bias or is illuminated by one or more suns. The device degradation is accelerated both if it is heated up at temperature higher than 60°C or if it is illuminated by several suns. When copper is used to make an ohmic contact, one has to be very careful in order to avoid any copper diffusion. For this reason, First Solar uses only 2nm of Cu onto a CdTe etched surface to make the back contact on its CdTe/CdS thin film solar cells [8].

In the past, in order to avoid any degradation, we did not use any copper, but we used a low gap p-type material, namely Sb₂Te₃ [9]. This compound exhibits a very low resistivity, on the order of $10^{-4}\Omega$ ·cm. If this material is deposited by sputtering at a substrate temperature around 300°C, it can make a good contact with CdTe and can give solar cells with an efficiency close to 16%. This type of contact resulted to be very stable even when the device is illuminated by 10-20 suns and at a temperature higher than 100° C. However, in some cases, depending on the starting Sb₂Te₃ target, the presence of a roll-over in the I-V characteristics has been found, indicating that some rectification, even if not very much pronounced, is present in the back contact.

In this paper we present a novel contact, that, despite it contains Cu, maintains the stability of the device and does not present any roll-over in the I-V characteristics.

2 EXPERIMENTAL DETAILS

The structure of the CdTe/CdS thin film solar cell used in our experiments is shown in Fig. 1. All layers, excluding CdTe that is deposited by Close Spaced Sublimation, are deposited by sputtering [9].

The novel contact is constituted by a layer of As_2Te_3 deposited directly onto the CdTe surface without any etching of CdTe, followed by a thin layer of Cu deposited onto As_2Te_3 at a substrate temperature of about 200°C. As_2Te_3 is a p-type semiconductor that has a forbidden gap of about 0.6eV and exhibits a room temperature resistivity of $10^{-3}\Omega$ ·cm. It melts at 360°C and can evaporate at temperature higher than 250°C in vacuum.

The As_2Te_3 thickness can be varied between 100 and 300nm while the Cu thickness can be varied between 2 and 20nm. As_2Te_3 can be deposited at a substrate temperature between RT and 200°C, while Cu has to be deposited between 100 and 200°C substrate temperature in order to get a good contact.

In our experiments, both As_2Te_3 and Mo are deposited by sputtering, As_2Te_3 with a deposition rate between 10 and 20Å/sec and Cu with a depositon rate of 5Å/sec. If both As_2Te_3 and Cu are deposited at room temperature, the contact is rectifying as one can see in Fig. 2, curve a.

Here the "roll-over" is clearly visible in the first quadrant of the I-V characteristic.



Figure 1: Structure of the CdTe/CdS thin film solar cell



Figure 2: J-V characteristic of a CdTe/CdS solar cells in which the back contact is deposited with different substrate temperatures: (*a*) $As_2Te_3 + Cu$ both deposited at room temperature; fill factor = 0.57, (*b*) $As_2Te_3 + Cu$ both deposited at 200°C; fill factor = 0.7

If Cu is deposited at a substrate temperature around 200°C, the "roll-over" disappears and the fill factor is much higher (Fig. 2, curve b).

In order to understand the behaviour of the double layer As_2Te_3+Cu , some samples were prepared by depositing As_2Te_3+Cu directly on glass with Cu deposited at 200°C substrate temperature. Besides, some samples were prepared by depositing onto As_2Te_3 a Cu layer up to 20nm thick, while other samples were prepared by depositing a 50nm thick layer. In all cases the thickness of As_2Te_3 was 200nm. These samples were analyzed by X-rays and were compared with samples containing only As_2Te_3 .

As one can see in Fig. 3 and 4 curves a and b, the samples containing Cu up to 20nm exhibit several Cu_xTe phases with $1 \le x \le 1.4$, while the samples containing 50 nm of Cu exhibit also the Cu₂Te phase. Back contacts on CdTe/CdS thin film solar cells made by using 50nm of Cu resulted to be not much stable, while cells made with 20nm or less of Cu resulted to be very stable and more efficient. This is in accord with what is reported by Wu and al. [7], that is, the Cu_xTe phases with x > 1.4 are not stable. A CdTe/CdS thin film solar cell, in which the back contact has been done by depositing, in sequence, at a substrate temperature of 200°C, 200nm of As₂Te₃ and 20nm of Cu, is shown in Fig. 2, curve b. No etching of CdTe has been done.



Figure 3: XRD analysis of (*a*) 200nm thick As_2Te_3 deposited on glass at 200°C substrate temperature, (*b*) 200nm thick As_2Te_3 film deposited on glass at 200°C substrate temperature on which 20nm thick Cu is deposited at the same temperature.



Figure 4: XRD analysis of (*a*) 200nm thick As_2Te_3 deposited on glass at 200°C substrate temperature (*b*) 200nm thick As_2Te_3 deposited on glass at 200°C substrate temperature on which 50nm thick Cu are deposited at the same substrate temperature.

Fill factor of this cell is ~ 0.7. The cell is stable even if a light soaking of 10 suns in the open circuit mode is done at a temperature of 100° C for 8 hours.

In order to further understand the As_2Te_3+Cu double layer behaviour, some experiments have been done by substituting As_2Te_3 with Sb_2Te_3 . In this case, the substrate temperature was varied between 200 and 350°C both for Sb_2Te_3 and Cu. In all the finished cells the back contact was not stable even if the Cu thickness was only 2nm. The cell efficiency is quite high at the beginning, but decreases very fast.

3 CONCLUSION

The results above reported can be explained in the following way. When Cu is deposited onto As_2Te_3 at a sufficiently high temperature, namely 200°C, Cu makes a solid state reaction with As_2Te_3 in which Cu substitutes As forming Cu_xTe. Depending on both As_2Te_3 and Cu

thickness, Cu_xTe phases with $x \le 1.4$ or x > 1.4 can be formed. The stable phase with $x \le 1.4$ can be formed by using an As₂Te₃ thickness of 200nm and a Cu thickness of 20nm or less at a substrate temperature around 200°C. This type of reaction cannot happen if Sb₂Te₃ is used instead of As₂Te₃, since Sb₂Te₃ is a much more stable material than As₂Te₃. With Sb₂Te₃, Cu remains free and diffuses into the CdTe/CdS structure, damaging the cell. This novel method of making the back contact on CdTe is similar, in some aspects, to the one commonly used in which first a Te-rich surface is created by means of a chemical etching of CdTe and than a very thin layer of Cu is deposited in order to form the Cu_xTe with $x \le 1.4$. However, a substantial difference is in the fact that, in our case, no etching of the CdTe is done since we do not need a Te- rich surface (this is substituted by As₂Te₃) and that a Cu thickness ten times higher can be used. This renders less critical the formation of the non rectifying contact giving a good stability to the CdTe/CdS thin film solar cell. This novel contact has been patented [10].

4 ACKNOWLEDGMENTS

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5 REFERENCES

- [1] D. Bonnet and P.V. Meyers, J. Mater. Res. 13 (1998) 2740-2753.
- [2] D.W. Miles, X. Li, D. Albin, D. Rose, T. Gessert, P. Sheldon, Prog. Photovolt. 4 (1996) 225-229.
- [3] W.J. Donaher, L.E. Lyons, G.C. Morris, Appl. Surf. Sci., 22-23 (1985) 1083-1090.
- [4] A. Rohatgi, R. Sudharsam, S.A. Ringel, M.H. Mac Dougal, Sol. Cells. 30 (1991) 109-122.
- [5] D.H. Rose, F.S. Hassoon, R. G. Dhere, D.S. Albin, R.M. Ribelin, X.S. Li, Y. Mahathongdy, T.A. Gessert, P. Sheldon, Prog. Photovolt. 7 (1999) 331-340.
- [6] S.H. Wei, S.B. Zhang, A. Zunger, J. Appl. Phys. 77, 9 (1995) 4489-4493.
- [7] X. Wu, J.Zhou, A. Duda, Y. Yan, G.Teeter, S. Asher, W.K. Metzger, S. Demtsu, Su-Huai Wie, R. Noufi, Thin Solid Films (2006), in press
- [8] C. R. Corwine, A.O. Pudov, M. Gloeckler, S.H. Demtsu, J.R. Sites, Sol. Energy Mat. & Solar Cells 82 (2004) 481-489.
- [9] N.Romeo, A. Bosio, V. Canevari, A. Podestà, Solar Energy 77 (2004) 795-800.
- [10]Patent nr. PCT/IT2007/000469