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GaN/Cu_2O heterojunctions for photovoltaic applications

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Abstract

Several growth methods were employed to investigate the photovoltaic behavior of GaN/Cu_2O heterojunctions by depositing cuprous oxide thin films on top of gallium nitride templates. The templates consist of a thin layer of GaN:Si grown on a sapphire substrate by metal organic vapor deposition. The deposition procedure was followed up by photolithographic structuring and thermal evaporation of metal contacts. For device characterization, J-V characteristics and external quantum efficiency were measured, pointing to a possible energy barrier in the conduction band. To gain further insight X-ray photoelectron spectroscopy was applied.

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Keywords: copper oxide; cuprous oxide; heterojunction; photovoltaics

1. Introduction

Due to its high absorption coefficient, non-toxicity and the abundance of its composing elements, cuprous oxide (Cu_2O) is a promising absorber material for photovoltaic applications, even despite of the relatively large band gap (2.17 eV). With increasing success in the past decade, more attention has been paid to zinc oxide/cuprous oxide heterojunctions, especially when oxidized copper foils, resulting in cuprous oxide substrates with superior electrical properties, are employed [1,2,3]. At forward bias, however the large conduction band offset of 1.0 eV

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limits the open circuit voltage: the theoretically attainable efficiency is decreased by about 50%. As a way out, we chose Gallium nitride as window layer: it offers a conduction band offset of 0.2 eV in relation to Cu_2O [4].

2. Experimental

The gallium nitride films were grown on polished sapphire substrates via MOCVD and were provided by the OSRAM AG. The cuprous oxide thin films were produced via RF-magnetron sputtering, deposited at 75 W, utilizing a copper target. An Argon flow of 35 sccm and oxygen flow of 3.4 sccm for the deposition at room temperature, 50 sccm Ar and 3.4 sccm O_2 for the deposition at 920 K, was used, corresponding to 4.5E-3 mbar and 7.5E-3 mbar in total pressure, respectively. Further films were produced by rapid thermal annealing (RTA) at 800 K after sputter deposition at room temperature, via chemical vapor deposition at 40 mbar, employing the evaporation of CuI_2 at a rate of 30 mg/h, transported by 1.4 slpm of argon flow under addition of 3 sccm oxygen flow at a temperature of 770 K, and plasma assisted molecular beam epitaxy at 5E-6 mbar, evaporating copper at 1350 K and adding 0.45 sccm of oxygen flow, where the plasma was powered with 250 W. After deposition, photolithographic processing steps were undertaken. That includes usage of diluted nitric acid and several soft-bake steps at 100 °C, as well as one hard-bake step at 100 °C for one hour, followed by the deposition of Ti/Au and Au metal contacts via thermal evaporation. J-V characteristics EQE were measured by a Keithley 4200SCS parameter analyzer, combined with a Xe arc lamp, monochromator, and AM1.5g filter. XPS measurements were carried out with a PHI Electronics VersaProbe II system. Film thicknesses were obtained from the interference of UV-VIS reflectance measurements; Grain sizes were determined atomic force microscopy. DC-Hall-effect was measured using insulating substrates, such as sapphire, magnesium oxide or quartz glass.

heterostructure	Film thickness (nm)	Avg. grain sizes (nm)	Hall mobility (cm^2/Vs)
PVD (3.1 sccm O_2)	540	50	<5
PVD (3.2 sccm O_2)	540	50	8
PVD (3.3 sccm O_2)	540	50	<5
PVD (3.4 sccm O_2)	540	50	<5
PVD (3.5 sccm O_2)	540	50	<5
PVD (3.4 sccm O_2, RTA)	540	50	10
PVD (920 K)	500	500-2000	52
CVD	720	500	22
MBE	160	500-1000	70

3. Results and discussion

On changing the oxygen flow applied when depositing Cu_2O via sputtering, the stoichiometry is significantly changed, the amount of intrinsic defects, causing p-type conduction, i.e. copper vacancies, can be controlled resulting in hole densities of 5E14 cm^{-3} up to 5E16 cm^{-3}, while staying within reasonable stoichiometric limits of the cuprous oxide phase [5]. The observed short circuit current densities in Fig. 1 show a maximum at 3.2 sccm oxygen flow during growth, which can be attributed to the carrier mobility that is slightly higher for lower oxygen flows. The open circuit voltage is significantly higher at an increased oxygen flow of 3.4 sccm, corresponding to higher carrier densities. A large open circuit voltage, combined with a very small short circuit current, is characteristic for an energy barrier at the interface, which will severely impede the minority carriers, i.e. electrons generated in the cuprous oxide absorber, to reach the gallium nitride emitter. That, in conjunction with the low

carrier mobilities, which originate in the small grain sizes, when sputter depositing at low temperatures, also accounts for a small diffusion length, resulting in the overall low quantum efficiency.

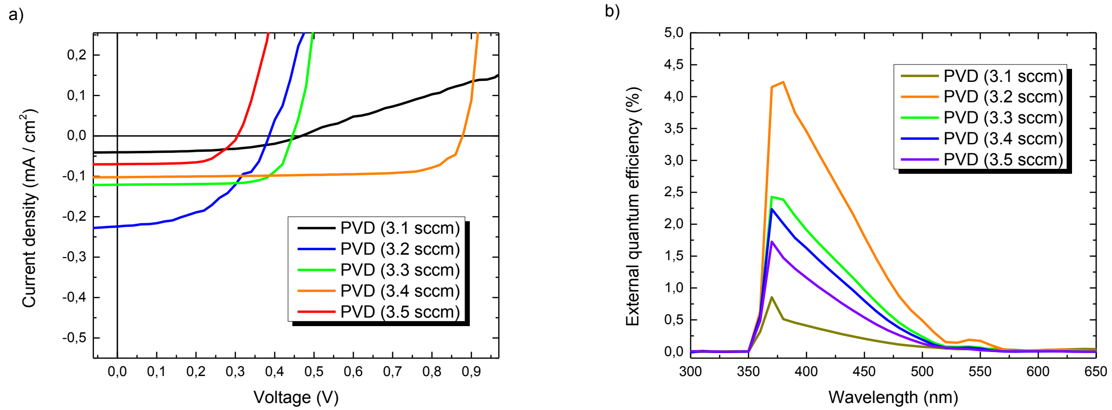

Figure 1: (a) J-V-characteristics of the heterostructures employing RF magnetron sputtering at room temperature under AM1.5g illumination at 100 mW/cm². (b) Corresponding external quantum efficiency measurements.

Table 1. Parameters of the devices with Cu_2O layers prepared by sputtering at room temperature.

heterostructure	V_{OC} (V)	J_{SC} (mA/cm²)	FF (%)	Efficiency (%)
PVD (3.1)	0.47	0.04	53	0.01
PVD (3.2)	0.39	0.22	46	0.04
PVD (3.3)	0.45	0.12	74	0.04
PVD (3.4)	0.87	0.10	78	0.07
PVD (3.5)	0.31	0.07	64	0.01

In order to investigate the possibility of an electron barrier in the conduction band, XPS measurements of a heterostructure deposited at room temperature via sputtering were undertaken. In Fig. 2 on the left hand side (a) a depth profile of the heterostructure XPS-spectra is depicted, showing the gallium $2p_{3/2}$ signal, clearly undergoing a shift in binding energy from a nitrogen bond towards an oxygen bond. The profile was collected by sequential sputtering and measuring. Each step corresponds to approximately 0.5 nm in depth. The graph on the right hand side (b) depicts the energetic positions of the $2p_{3/2}$ maxima for each, gallium and copper. Since the measurement was performed insulated with a constant neutralization of 1.6 eV it is prone to error, due to an occasional charge up, leading to energetic shifts that could be misinterpreted as a change in binding energy. That however would cause all signals to shift in the same manner, which is not the case in the interface region.

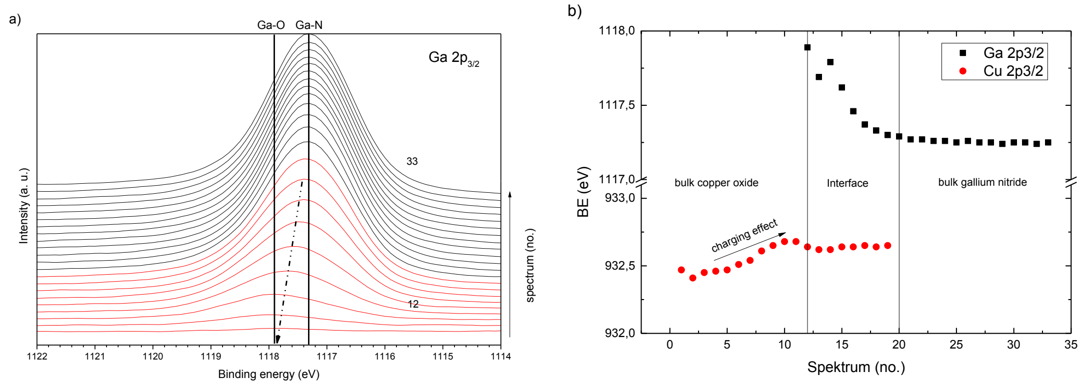

Fig. 2: XPS depth profile of a heterostructure prepared by sputtering at room temperature. (a) Partial spectra showing the Ga $2p_{3/2}$ signal, where the interface region is depicted in red. (b) The peak positions of each, the Ga $2p_{3/2}$ and the Cu $2p_{3/2}$ signal.

When heat is applied, during or after sputter deposition, the short circuit current is significantly increased, while the open circuit voltage is decreased. Although an improved quality of the absorber material can be reached at annealing temperature ranges from 1200 K and higher, the thermal annealing was performed at 800 K and will only cause marginal changes to the cuprous oxide film. Thus, a change at the hetero interface can be concluded. Heating during the sputtering process results in improved material quality and therefore in increased minority carrier diffusion lengths, as is observed in the electrical measurements.

In addition to sputter deposition other growth methods, such as chemical vapor deposition and plasma assisted molecular beam epitaxy were employed. While the chemical vapor deposition, being the least damaging deposition technique, shows the largest short circuit current, the open circuit voltage and parasitic resistances obtained, were the overall worst. That can be explained by the very low growth rate of approximately 5 nm per hour. The material properties of the absorber film fabricated by PAMBE are superior to the other growth methods used. However, a film thickness of only 160 nm could be reached, which is caused by a significantly lowered growth rate on the GaN-templates as compared to other substrates, such as MgO. Thus, the external short circuit current and quantum efficiency did not exceed the ones of the devices involving sputtering at high temperatures or chemical vapor deposition.

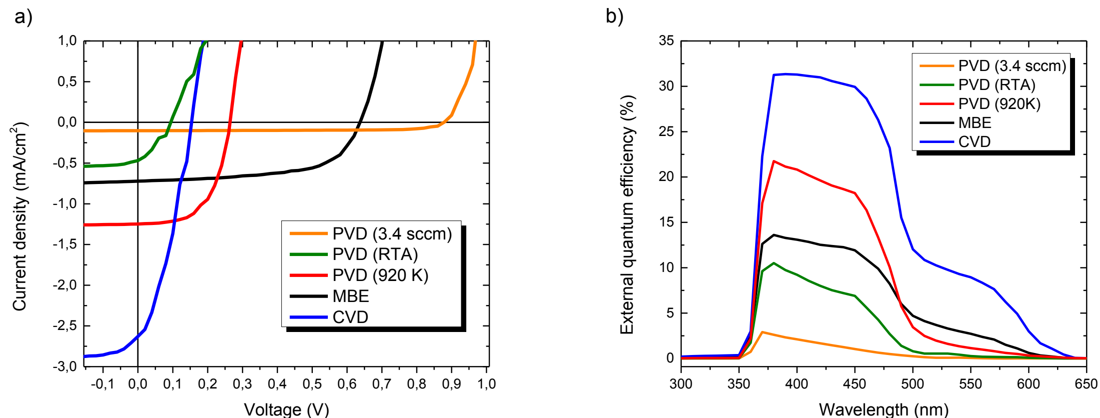

Fig. 3: (a) J-V-characteristics of the remaining heterostructures under AM1.5g illumination at 100 mW/cm^2. To ease comparison the device prepared by sputtering at room temperature and 3.4 sccm O_2 flow was added. (b) Corresponding external quantum efficiency measurements.

Table 2. Parameters of the remaining devices.

heterostructure	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	Efficiency (%)
PVD (RTA)	0.1	0.47	28	0.01
PVD (920 K)	0.27	1. 25	57	0.19
PVD (MBE)	0.64	0.72	61	0.28
PVD (CVD)	0.15	2.63	35	0.14

4. Conclusion

Given the results of the films sputtered at room temperature, it may be concluded that electrical material properties of those low temperature absorber films are too inferior to permit reasonable photovoltaic conversion efficiencies. Also a strong energy barrier in the conduction band can arise. XPS measurements point to a gallium oxide layer, possibly a delafossite, i.e. $CuGaO_2$, which could impose the electron barrier at the hetero interface. Gallium oxide forming a barrier would contradict the results recently published by Minami et al. [6], successfully employing a Ga_2O_3 window layer, leaving $CuGaO_2$ or a strong interface dipole as the only candidates. However, further investigation to clarify the latter must be undertaken. Furthermore, it can be concluded that recombination at the hetero interface is strong in any case. It is therefore safe to say that further investigation should focus on the hetero interface properties and might show the necessity for a buffer layer to overcome interface recombination. It should be noted that sufficient hole densities from intrinsic defects in cuprous oxide require huge quantities of copper vacancies, due to their large energetic depth and that the donor density in the gallium nitride templates used are too low, preventing a beneficial asymmetric development of the space charge region further into the cuprous oxide absorber layer.

5. Acknowledgements

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6. References

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