Influence of the N\textsubscript{2} gas flow on optical and structural properties of reactively sputtered ZrN films

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Abstract. We present optical and structural properties of reactively sputtered zirconium nitride (ZrN) films for application as back reflectors in Cu(In,Ga)Se\textsubscript{2} solar cells with sub-micrometer absorbers. In this study, ZrN films were deposited by reactive DC sputtering on blank, Mo-coated and Zr-coated soda-lime glass at two different process pressures and various ratios of nitrogen mixed in the argon working gas. When characterised by x-ray diffraction (XRD), the majority of the films were found to consist of single-phase cubic ZrN. All peaks corresponding to the ZrN phase were present in the diffractograms with intensities similar to those obtained from bulk ZrN, indicating that the films were randomly oriented. No significant differences were found between films grown on different substrate types. Films sputtered with lower nitrogen partial pressures displayed a spectral optical reflectance similar to metallic Zr, while films prepared with higher N\textsubscript{2} flows showed the pronounced Drude-like reflectance characteristic of the nitride. The best ZrN films were achieved with a process pressure of 2.5 mTorr and a N\textsubscript{2}/(Ar+N\textsubscript{2}) flow ratio of 26.5%. At a wavelength of 800 nm the reflectance of these reached 85%, as compared to a typical value of 58% in the case of molybdenum.

1. Introduction
Zirconium nitride (ZrN) films have previously been proposed to replace molybdenum films as back contacts for Cu(In,Ga)Se\textsubscript{2}-(CIGS-)based solar cell devices with CIGS absorbers thinner than one micrometer.[1] The rationale for this is that thin devices on molybdenum back contacts typically suffer from efficiency losses in the order of up to 20% (relative) compared to cells with 2-\textmu m thick absorbers. These losses are caused on the one hand by incomplete absorption of the incident light by the CIGS absorber, which in a 0.5-\textmu m thick absorber becomes prominent for wavelengths exceeding 700–800 nm; on the other hand by the moderate reflectance of molybdenum, which measured in air is about 58% at 800 nm. In contrast to this, zirconium nitride exhibits a stronger long-wavelength reflectance than Mo. Thus more light not absorbed on the first pass will traverse the absorber a second time, which reduces the absorption losses and leads to higher efficiencies in this type of excessively thin solar cells.

2. Experimental
Table 1 lists the deposition parameters for the investigated samples. Zirconium nitride (ZrN) films were deposited by DC magnetron sputtering from a 150-mm diameter zirconium target in Ar–N\textsubscript{2} reactive gas mixtures using a von Ardenne CS 730S sputtering system. The preparations were conducted on two kinds of substrates: on blank soda-lime glass (SLG) and on SLG coated with a 300-nm film of molybdenum. The sample dimensions were 100 by 100 mm in all cases,
Table 1: The samples considered, and the main process parameters used for their preparation. ID designates the letter by which the samples will be identified throughout this paper.

| ID | Substrate type | Pressure [mTorr] | N$_2$ flow [sccm] | N$_2$: (Ar+N$_2$) flow ratio [%] | ZrN sputter duration [s] | Approx. ZrN thickness [nm] |
|----|----------------|------------------|-------------------|-------------------------------|------------------------|--------------------------|
| A  | Zr             | 5                | 20                | 16.7                          | 30                     | 150                      |
| B  | Zr             | 5                | 24                | 19.4                          | 30                     | 100                      |
| C  | Zr             | 5                | 30                | 23.1                          | 30                     | 80                       |
| D  | Zr             | 5                | 36                | 26.5                          | 30                     | 60                       |
| E  | Zr             | 5                | 24                | 19.4                          | 30                     | 90                       |
| F  | Mo             | 2.5              | 18                | 26.5                          | 400                    | 870                      |
| G  | glass          | 2.5              | 18                | 26.5                          | 400                    | 900                      |

with a glass thickness of 1 mm. The samples were loaded onto the process chamber’s rotary table in batches of four by way of a load-lock system. After pumping to a base pressure well below $1\cdot10^{-6}$ Torr, argon gas was admitted into the chamber, and the process pressure was controlled to a preset value of either 2.5 mTorr or 5 mTorr. The argon flow was chosen according to the desired pressure, to 50 sccm for 2.5 mTorr and to 100 sccm for 5 mTorr. When the pressure had stabilised, the plasma was ignited at a power of 1500 W and the target was sputter-cleaned for five minutes. For a majority of the blank glass samples, this was followed by the deposition of a metallic Zr primer, lasting 10 seconds and yielding a film approximately 100 nm thick. In Table 1 these are designated by the sample type ‘Zr’. The fabrication of the ZrN layer was then initialised by a brief conditioning of the target in an argon-nitrogen atmosphere with the intended N$_2$/(Ar+N$_2$) flow ratio $F(N_2)$, followed by the deposition on the samples. No external heating was applied to the samples.

The films A—D were deposited in direct sequence in one batch, with about five seconds of target conditioning after each new nitrogen flow was set. Sample E was fabricated with the same process parameters as sample B, but as for sample A the deposition followed nearly directly upon the sputter cleaning of the target. The preparation of samples F and G included an effective conditioning time of about 200 s.

After sputtering, the crystal structure of the films was characterised by both Θ–2Θ and grazing-incidence x-ray diffraction (XRD) scans in a Philips X’pert MRD equipped with an x-ray mirror and a parallel-plate collimator and using the Cu-K$_\alpha$ radiation. Specular reflectance spectra were recorded at near-normal incidence in a single-beam spectrophotometer[2], in the wavelength range of 350–2500 nm (of which the range up to 1100 nm is of interest for solar-cell applications).

3. Results and Discussion

Grazing-incidence XRD diffractograms of five of the samples from Table 1 are shown in Figure 1. All films grown with a value of $F(N_2)$ above 19% (as demonstrated by samples B–E) show significant XRD reflections only at the positions corresponding to crystal planes of ZrN, from which we conclude that these zirconium-nitride films consist of single-phase cubic ZrN. Small peaks belonging to the (101) and (103) planes of hexagonal Zr do appear in the samples B and C (at $2\Theta \approx 36.5^\circ$ and $\approx 63^\circ$). However, when the incident angle is lowered further, thus reducing the penetration depth, the last traces of these peaks disappear while the ZrN reflections are still present. This indicates that the Zr peaks belong to the Zr bottom layer and are no evidence for a phase mixture in the topmost film.

Moreover, we view the films to be polycrystalline and randomly oriented, as is signaled by the fact that peaks corresponding to all the crystal planes of ZrN occur in the diffractograms with
intensities comparable to those obtained from bulk ZrN. θ–2θ scans point to a fairly random orientation as well, showing a weak tendency towards a (111) preferred orientation of the ZrN.

Finally, with the increasing nitrogen flow in samples B through D, we observe a small shift of the ZrN-peak positions towards smaller angles in 2θ, both in grazing-incidence and in θ–2θ XRD scans. As Benia et al. [3] suggest, this can probably be attributed to the unit cells of the stoechiometric compound being dilated by inclusion of nitrogen atoms.

The XRD graphs of the films fabricated on different samples – film F being deposited on molybdenum, and film G directly on glass – are very similar to that of sample D, both in peak intensities and in peak positions. Sample D is grown at the same value of $F(N_2)$ but at the higher of the two pressures investigated. This finding implies that the substrate material does not have a perceivable influence on the structure of the ZrN films.

Sample A contrasts strongly with the other samples investigated in this study. As documented in Table 1, this film was grown at the lowest nitrogen flow value in this series, and as mentioned above, the conditioning time was with only five seconds. The diffractogram in Figure 1 displays reflections from the ZrN phase which have reduced intensities and at the same time are smeared out and blending with nearby reflections from Zr, which in turn are about an order of magnitude stronger than in the other cases. This indicates that the film in sample A consists of a Zr/ZrN phase mixture and also has a lower crystallinity than the rest. The peculiarity of sample A is also seen in the reflectance spectra depicted in Figure 2, which we consider next.

To begin with, we observe that the samples B through D and F share the principal form of the reflectance profile that is characteristic of ZrN films and is well described by the free-electron Drude model.[4] With the increase in nitrogen flow from sample B to D, the long-wavelength reflectance diminishes, yielding a colour shift from golden to brownish. Figure 2 does not include the samples E and G, which have Drude-like profiles staying slightly below those of samples C and F, respectively.

With regard to sample A, it is remarkable that the reflectance matches much more that of the silver-grey Zr metal than that of the other ZrN samples, with just a weak, gradual drop in the short-wavelength region. This supports the conclusion that sample A is a mixture of Zr and ZrN. However, it is doubtful whether the observation can be directly correlated to the low
nitrogen flow as the situation is complicated by the short conditioning time. Because of this it is rather likely that the target did not reach the steady-state condition of ZrN compound mode before the ZrN deposition started, and possibly neither throughout the 25-second deposition. This issue shall be investigated in detail in a follow-up study.

One effect of the difference in $F(N_2)$ can be noted with the data at hand, though, in comparing samples A, B, and E. As told above, the only difference in the preparation of samples B and E was the time elapsed since the sputter cleaning of the target; sample B was preceded by another deposition, albeit at a lower flow, while sample E was not. In effect, except for smaller peak intensities, the diffractogram of sample E in Figure 1 resembles that of sample B and shows no traces of a Zr phase, and likewise the reflectance is reduced (by ca. 6% at 800 nm) but otherwise Drude-like. Both these statements are not true for sample A, as discussed above. Thus one can conclude that the compounding of the target proceeds at considerably different rates depending on the nitrogen flow, such that a total of 35 seconds is sufficient for complete compounding at $F(N_2)$ above 19%, while it is not at values below.

4. Conclusion
Investigating zirconium-nitride thin films prepared by reactive sputtering, we have found a markable influence of the nitrogen gas flow, but no significant differences between films grown on different substrate types. Films fabricated at low $N_2$ flows displayed an optical reflectance similar to metallic Zr. With flows over a certain threshold, films showed the pronounced Drude-like reflectance characteristic of the nitride. XRD measurements confirmed that the latter films consisted of single-phase ZrN, but that the former were made up of a Zr/ZrN phase mixture. While optically very good, golden ZrN films were achieved at intermediate nitrogen flows, further increases in nitrogen flow would yield less reflective and brownish films.

References
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