Ion Beam Assisted Sputter Deposition of ZnO for Silicon thin film Solar Cells

M Warzecha1*, D Köhl2, M Wuttig2, J Hüpkes1

1IEK5-Photovoltaik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany
2Institute of Physics (IA), RWTH Aachen University, Sommerfeldstraße 14, 52074 Aachen, Germany

*j.huepkes@fz-juelich.de

Abstract. Ion Beam Assisted Deposition (IBAD) is a promising technique for improved material quality of ZnO-based thin films. The operation of an auxiliary Ar+ ion source during deposition of ZnO:Ga thin films by dc magnetron sputtering led to improvement in crystalline texture, especially at low temperatures due to momentum transfer from the ions to the growing film. Etching of IBAD-ZnO:Ga films in diluted HCl revealed crater like surface structures with crater diameters of up to 600 nm. These structures are usually achieved after deposition at high substrate temperatures. This is an indication that the grain structure was remarkably changed by bombarding these films during deposition in terms of increasing the compactness of the ZnO:Ga films. Subsequent annealing procedures led to improvement in the electrical and optical properties. Hydrogenated microcrystalline silicon (µc-Si:H) solar cells exhibited enhanced efficiency as compared to cells on other low-temperature sputtered reference ZnO films. This improvement was ascribed to light trapping by the modified etching behaviour of the IBAD-ZnO:Ga films as well as improved transparency after the vacuum annealing step.

1. Introduction
Zinc Oxide has attracted much attention as a transparent conducting oxide (TCO) for a variety of applications, such as flat panel displays or as front contact for thin film silicon solar cells [1,2]. The most popular TCO materials for thin film solar cells is Aluminum-doped ZnO (ZnO:Al), but Gallium offers some advantages over Al: The similarity of the ionic radii between Zn and Ga should result in small lattice deformations only [3]. In addition, Ga is less reactive and thus more resistive to oxidation compared to Al [4]. Previously, the crystalline quality of ZnO films has been largely improved by bombarding the films with Xe+-ions from an auxiliary ion gun during a reactive sputter process [5].

A good light scattering ability of the front contact is necessary to increase the path length of the incoming light into the thin film silicon solar cells [6]. This is realized by roughening the surface of the ZnO thin films in diluted hydrochloric acid. However, the feature sizes and shapes after etching are highly sensitive to the substrate temperature during deposition [7]. Films with optimal surface topographies for light incoupling in the solar cell after TCO etching are characterized as type B material of the modified Thornton model by Kluth et al. [8]. However, high substrate temperatures are necessary to achieve such features. This high temperature deposition is accompanied by heating and cooling times and is one important cost factor in production of high quality ZnO films. Ion beam assisted deposition (IBAD) is a versatile technique to produce high quality films without additional substrate heating, allowing the deposition at room temperature (RT) conditions [5,9].
This article studies the IBAD at room temperature of ZnO:Ga thin films using Ar⁺-ions. Due to this additional momentum transfer, the ZnO:Ga film quality was improved [10]. Finally, the ZnO:Ga thin films were etched and applied as light scattering front contacts in silicon thin film solar cells.

2. Experimental

ZnO:Ga thin films were grown by IBAD using a four inch ceramic target and an inverse sputter etching tool ISE 90 (von Ardenne Anlagentechnik, Dresden, Germany) on Corning eagle XG glass substrates with a size of 10 x 10 cm². We simultaneously operated a ZnO:Ga-ceramic target (2 wt. % Ga₂O₃) in dc mode and the additional ion source by rf excitation in pure argon. The target and the ion source are arranged with an angle of 45° to the substrate normal, while the substrate was rotated at five rounds per minute during deposition.

The discharge power of the ZnO:Ga-target was kept constant at 100 W, whilst the power of the ion gun was varied between 0 W and 200 W. This resulted in a change in the bias voltage \( U_{bias} \) of the ion gun between 0 V and 640 V, changing the ion current density. High energy ions with energies between 1.5 keV and 2 keV escape through the extracting electrode of the ion source. During every negative half wave of the rf excitation electrons with energies in the range of 100 eV are accelerated to the substrate surface. Table 1 summarizes the bias voltages of the inverse ion etching tool of all samples during deposition. The first series was prepared at room temperature (RT). One sample experienced a bombardment during the initial growth stage only, i. e. after a film thickness of approximately 30 nm the ion source was switched off and the ZnO:Ga-target was operated solely until a total thickness of approximately 800 nm was achieved. All films were intended to have a film thickness of approximately 800 nm. Three films were reproduced (4th column) for deposition of hydrogenated microcrystalline Silicon solar cells on top of it. One of these films was subsequently annealed at a temperature of 450°C for 17 h in vacuum at a base pressure of \( 7 \times 10^{-5} \) Pa. For comparison, a film which was deposited at a substrate temperature of \( T_s = 250°C \) and additionally ion bombarded by IBAD was also added to the IBAD-series. The deposition pressure during growth was kept at 0.33 Pa and the Ar gas flow rate amounted to 10 sccm.

<table>
<thead>
<tr>
<th>Ion source power ( P ) [W]</th>
<th>Bias Voltage ( U_{bias} ) [V]</th>
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<tr>
<td>( T_s = RT )</td>
<td>( T_s = RT )</td>
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<tr>
<td>(30 nm IBAD seed)</td>
<td>for solar cells</td>
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<tr>
<td>0</td>
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<tr>
<td>20</td>
<td>180</td>
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<td>200</td>
<td>640</td>
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A Phillips X’Pert Pro diffractometer with CuKα radiation was used for X-Ray diffraction (XRD) measurements in the Bragg-Brentano geometry. The electrical properties were obtained by Hall effect measurements with a Keithley 926 Hall set-up, using the van der Paw method. Film thickness was measured using a surface profiler (Dektak 3030, Veeco Instruments Inc.) by scanning a step etched into the film with diluted hydrochloric acid (HCl, 2 w/w%). Optical properties were carried out by a double beam spectrometer (Lambda 19, Perkin Elmer). After deposition, the films were etched in diluted HCl (0.5 w/w%) for up to 15 s at room temperature to achieve textured surfaces. Transmission
measurements after etching were done without using CH$_2$I$_2$ as index-matching fluid, therefore internal light trapping reduces the transmission values in our studies [7]. The surface topography was analyzed by atomic force microscopy (AFM, Nanostation 300, S.I.S.). The deposition of hydrogenated microcrystalline silicon (μc-Si:H) solar cells was realized by plasma enhanced chemical vapor deposition (PECVD) in a reactor for substrates with a size of up to 30 x 30 cm$^2$. A ZnO:Al/Ag/ZnO:Al sputtered and laser scribed back layer serves as reflector and back contact. Details on the PECVD deposition process can be found elsewhere [11,12]. The solar cells were characterized by measuring the current-density-voltage ($j$-$V$) curves using a sun simulator (AM 1.5, 100 mW/cm$^2$, 25°C) on 1 x 1 cm$^2$ large cells. Quantum efficiency measurements were performed using the differential spectral response (DSR) technique at short circuit conditions. Using a filter wheel, the simulated sun light was separated in 21 spectral ranges between 350 nm and 1100 nm.

3. Results and discussion

3.1. Structural properties

Figure 1 shows X-ray diffraction patterns in a semi-logarithmic scale for room-temperature deposited IBAD-ZnO:Ga thin films, grown at different bias voltages between 0 V and 640 V of the inverse sputter etching tool. The reference sample, which did not experience additional ion bombardment (black, solid line) revealed a strong (002) diffraction signal at 34.30°, indicating that the films are c-axis oriented as it is commonly observed for sputtered ZnO:Al films [13,19]. This graph shows that ion bombardment with moderate bias voltages led to increase in the intensity of the diffraction peak until a maximum is reached at $U_{\text{bias}} = 270$ V (green, dashed). Further increase in the bias voltage up to $U_{\text{bias}} = 480$ V (orange, dot dashed line) revealed a strong shift of the now much broader diffraction peak and a decrease in diffraction intensity. At $U_{\text{bias}} = 560$ V (purple, short dashed line) and...
$U_{\text{bias}} = 640 \text{ V}$ (grey, dotted line), respectively, the effects are even stronger and the signal intensity significantly diminishes below that of the reference sample, indicating that the preferentially oriented crystalline order is reduced at such high ion energies.

For comparison, a film, which was grown at a higher substrate temperature ($T_s = 250^\circ\text{C}$, blue, short dashed dotted line) and a room-temperature sputtered ZnO:Ga film with an IBAD seed layer of 30 nm (red, long dashed line) are also included in this graph. The deposition at high substrate temperatures ($T_s = 250^\circ\text{C}$) led to significant increase in the intensity by more than one order of magnitude, indicating that high temperature deposition led to improved texture. An IBAD seed layer of 30 nm thickness showed increased peak intensity by a factor of two in comparison to the reference sample.

A shift of the peak position is observed with increasing $U_{\text{bias}}$. This hints to stresses induced into the IBAD-ZnO:Ga films, which is caused by peening due to the high energy ion bombardment [14,15]. At high bias voltages ($U_{\text{bias}} > 560 \text{ V}$) an additional shoulder appears approximately at the peak position of the reference sample. This is interpreted as a phase separation at high strain conditions with some crystallites showing relaxation to the unstrained lattice.

Figure 2 displays the (002) peak position, determined from Figure 1 via peak fits, in dependence on the bias voltage for IBAD-ZnO:Ga-films. The upper axis in this figure roughly represents the applied power of the ion gun during deposition as an additional parameter. On the right y-axis, the calculated c-lattice parameter is illustrated. The seed layer sample is indicated by a red circle, while the high temperature samples are marked by blue triangles. Due to the double peak structure at high bias voltages the estimation of the peak position by using a software fit is hindered, therefore higher error bars resulted for these data points. ZnO:Ga-films deposited at low bias voltages showed almost no change in peak position. For $U_{\text{bias}} > 180 \text{ V}$ the peak shifts monotonously to smaller angles, resulting in a total shift of up to $1^\circ$ at $U_{\text{bias}} = 640 \text{ V}$. Also indicated is the peak splitting at $U_{\text{bias}} = 580 \text{ V}$ and...
$U_{\text{bias}} = 640$ V. In correlation to the peak shift, the c-lattice parameter increases from 5.229 Å to 5.384 Å. This corresponds to a strain of about 3.0 % in c-lattice direction caused by compressive stress of up to -7.0 GPa in comparison to the reference RT grown sample [16]. Phase separation, as marked by the peak splitting in Figure 2, occurred at a stress of ~6.5 GPa. According to Desgreniers [17] the phase separation at room temperature should occur at a strain of about -9 GPa. However, the growth at high substrate temperatures can reduce the phase transformation point to smaller strain values [18]. The additional bombardment, could be responsible for the reduced phase separation point in our experiment. Kappertz et al. [19] observed coexistence of relaxed and strained phases also at a stress of -5 GPa. This value is consistent with our results.

The IBAD-ZnO:Ga sample with a 30 nm seed layer reveals no significant change in the peak position compared to the reference, room-temperature grown sample. However, the peak intensity is slightly higher. High temperature deposition reveals a peak position at 34.45°, which shifts to 34.20° due to ion bombarding at $U_{\text{bias}} = 310$ V. This corresponds to a reduced c-axis parameter by 0.7 %.

As the Full Width at Half Maximum (FWHM) is related to the size of the coherently diffracting regions in the films, Figure 3 (a) shows the FWHM of the 2Θ diffraction peaks and (b) shows the average vertical grain size ($L$) in dependence on the bias voltage, calculated using Scherrer’s formula and under the assumption of perfect crystal grains [20]. A decrease in FWHM with increasing $U_{\text{bias}}$ is noticed, followed by a minimum of FWHM = 0.2° at $U_{\text{bias}} = 270$ V, which is consistent with the change in intensity, as shown in Figure 1. Further increase in $U_{\text{bias}}$ results in an increase of the FWHM. The average grain size shows an increase with increasing bias voltage and reaches a maximum of about $L = 41.3$ nm at $U_{\text{bias}} = 270$ V. This value is comparable to the grain size for the high temperature grown sample, which also shows a slight increase from 38.5 nm to 42.2 nm due to the additional bombardment. In correlation with the increase in grain size as the substrate temperature increases, as known from literature [21,22,23], here the grain size increases with increasing ion energy

![Figure 3](image-url). (a) Full Width at Half Maximum (FWHM) and (b) average grain size $L$ of IBAD-ZnO:Ga films as a function of bias voltage.
bombardment. This hints to the enhanced surface mobility of the incoming species, leading to improved arrangement of the crystal grains. Again, for the IBAD seed layer there is no change in FWHM compared to the reference, unbombarded ZnO:Ga film.

A slight increase in grain size to $L = 33.9$ nm is noticed for the IBAD-ZnO:Ga sample with a 30 nm seed layer as compared to $L = 30.8$ nm for the reference without ion bombardment during initial film growth. The increase in grain size stays in agreement with growth model introduced by Köhl et al. [9]: Due to the ion bombardment columnar growth of large and parallel grains, extending from the beginning of the substrate surface until the film surface is predicted. On the other hand, a nucleation zone consisting of small grains is suppressed, resulting in larger vertical average grain size. However, the values for the grain size are still much lower than for most ZnO:Ga films, treated by ion beam during the whole deposition process.

3.2. Electrical properties

Figure 4 shows electrical properties, (a) Hall mobility, (b) carrier concentration, and (c) resistivity of IBAD-ZnO:Ga thin films as a function of the applied bias voltage of the auxiliary ion gun. Again, the upper x-axis in this figure represents the applied power of the ion gun.

![Figure 4](image_url)

**Figure 4.** (a) Hall mobility, (b) carrier concentration and (c) resistivity of IBAD-ZnO:Ga thin films as a function of bias voltage of the ion source. The top x-axis shows the applied power on the ion source.

![Figure 5](image_url)

**Figure 5.** Hall mobility in dependence on the induced stress in IBAD-ZnO:Ga thin films.
Increasing the bias voltage leads to a continuous decrease in Hall mobility from 19.2 cm²/Vs to 11.3 cm²/Vs. The carrier concentration first remains at 3.7 x 10²⁰ cm⁻³ up to a bias voltage of 180 V. With increasing the bias voltage the carrier concentration reaches a minimum with 2.0 x 10²⁰ cm⁻³ at 480 V and then increases with increasing $U_{\text{Bias}}$. The resistivity therefore increases from 8.6 x 10⁻⁴ Ωcm and shows a maximum with 2.6 x 10⁻³ Ωcm at $U_{\text{Bias}} = 570$ V. In analogy to the XRD results, the ZnO:Ga sample with a 30 nm IBAD seed layer shows no change in mobility, carrier concentration and resistivity compared to the reference sample, which means that the seed layer does not influence the electrical properties. High temperature deposition shows mobility, carrier concentration and resistivity of 37.8 cm²/Vs, 5.5 x 10²⁰ cm⁻³ and 3.1 x 10⁻⁴ Ωcm, respectively. The additional bombardment during growth decreases mobility and carrier concentration to 18.2 cm²/Vs and 4.2 x 10²⁰ cm⁻³, respectively. The resistivity increases to 8.1 x 10⁻⁴ Ωcm. The deteriorated high-temperature sample shows mobility and resistivity, which are comparable to the room temperature grown reference sample without ion bombardment.

Usually, improved crystalline order and increase in grain size should result in enhancement of the mobility [24]. However, the mobility decreases with increasing the bias voltage. A possible reason for the deterioration in the electrical properties can be related to stress in the films. Figure 5 shows the dependence of the mobility on the calculated stress in the IBAD-ZnO:Ga thin films. It can be seen clearly that stress up to -2.4 GPa shows significant decrease in the mobility by 40 %. Further increase in stress rather leads to saturation at mobilities between 11 cm²/Vs and 12 cm²/Vs. Similar results with a reduction in mobility by about 79 % is found by Li et al. [25] for Ga-doped ZnO films stressed along the c-axis. Saturation at high stresses can be traced back to the phase separation, which limits the decrease in mobility. High temperature deposition and additional ion bombardment shows reduction in mobility by a factor of two, compared to the unstressed sample, which was deposited at $T_s = 250°C$. Due to high temperature deposition and high energy bombardment of films and due to the similar behavior compared to room temperature deposited films, the reduction in mobility might be related to stress in both cases.

3.3. Optical properties

Transmission spectra of several IBAD-ZnO:Ga thin films have already been shown elsewhere [26]. Selected transmission spectra are given in Figure 9(a). Figure 6 shows the average transmission $T_{\text{AV, VIS}}$ in the visible spectral range (λ = 400 nm to 800 nm) as well as the transmission in the near infrared region $T_{\text{AV, NIR}}$ (λ = 800 nm to 1100 nm) of IBAD-ZnO:Ga films in dependence of the bias voltage. In addition to the above mentioned series the average transmission of one film that was grown at room temperature and subsequently annealed at a temperature of 450°C for 17 h is included in this graph. The graph shows that increasing the bias voltage for IBAD-ZnO:Ga leads to increase of $T_{\text{AV, VIS}}$ from 63.6 % to 76.9 % and $T_{\text{AV, NIR}}$ from 66.7 % to 80.2 %, respectively. Low transmission values after deposition at room temperature conditions are observed, because of absorption due to defects (see Figure 3(a)). In correlation to the improved crystalline order, the transmission values increase with increasing $U_{\text{Bias}}$, but improvement in transmission is still seen above $U_{\text{Bias}} = 270$ V, although the crystal quality starts to deteriorate, indicated by increased FWHM. Reduction in absorption near sub band gap region can be a reason for increased transmission. This is a hint that the defect density induced by the ion bombardment is reduced by the annealing step, since sub-band gap absorption is usually ascribed to defects, dislocations or grain boundaries [27,28].
In correlation to the electrical properties, the IBAD-seed layer has no influence on the optical properties as compared to the reference unbombarded sample. High temperature deposition reveals highly transparent films with $T_{Av, VIS} = 81.8\%$ and $T_{Av, NIR} = 74.7\%$, respectively. The bombardment of these films during deposition decreases $T_{Av, VIS}$ slightly to 80.8\%, but leads to an increase for $T_{Av, NIR}$ up to 78.8\%. On the other hand, the post deposition annealing increases $T_{Av}$ in the whole spectral range, i.e., $T_{Av, VIS} = 78.2\%$ and $T_{Av, NIR} = 82.6\%$, respectively. This means, that the post annealed films are more transparent in the infrared range than the sample, which was deposited at high temperature. This improvement in transmission is related to increased sheet resistance from 3.7 $\Omega\cdot \square$ for high temperature deposition to 38.1 $\Omega\cdot \square$ for RT-deposition with subsequent annealing.

### Figure 6: Average transmission between 400 nm and 800 nm ($T_{AV, VIS}$), as well as between 800 nm and 1100 nm ($T_{AV, NIR}$) in dependence to the bias voltage for IBAD-ZnO:Ga films. The annealing of the RT-IBAD sample, grown at $U_{Bias} = 560\ V$, was done in a vacuum chamber for 17 h at 450°C.

### 3.4. Etching behaviour

To texturize the surface of the ZnO films, wet chemical etching was applied using diluted HCl (0.5 w/w%). The etching rate of the films in dependence on the bias voltage is shown in **Figure 7**. Whilst the etching rate is almost constant at about 10 nm/s in the range between $U_{Bias} = 0\ V$ and 180 V, a significant increase in the etching rate to a value of about 58 nm/s is noticed at high $U_{Bias}$. This means a change in the etching rate by a factor of almost six. A drastic increase in the etching rate from 1.7 nm/s to about 17.4 nm/s is also noticed for the sample, which was deposited at $T_s = 250^\circ\ C$, meaning an increase by a factor of more than ten. Again, the 30 nm IBAD seed layer has no influence on the etching rate, revealing an etching rate of 9.6 nm/s, which is comparable to the reference sample.
**Figure 7.** Etching rate in dependence to the bias voltage for IBAD-ZnO:Ga films. The black line is inserted to guide the eye.

**Figure 8** shows AFM surface topographies of several IBAD-ZnO:Ga films, grown at different bias voltages after etching in diluted HCl etch conditions. The corresponding RMS roughness values are given underneath each image. The film that was grown at $U_{\text{Bias}} = 0$ V represents material with relatively low compactness [8] consisting of small and steep craters with an average lateral feature size below 300 nm. With increasing the bias voltage to 480 V features become larger and craters with a lateral size of 600 nm are randomly distributed over the surface. Further increase in the bias voltage reveals a surface topography with small features. The RMS roughness increases with increasing bias voltage from 70 nm without bombardement (0 V) to a maximum of 131 nm at 570 V. Then, it reduces to 67 nm at the highest bias voltage of 640 V. ZnO films with low compactness, which lead to small etch features at high etch rates are usually achieved after deposition at low temperatures, films with large and wide craters are found after etching of ZnO films that were grown at high substrate temperatures [7]. High etching rates are indication for less compact material, while low etch rates and large crater structures appear after etching of highly compact films. The change in feature sizes of our IBAD-ZnO:Ga thin films indicate that the compactness changed due to additional bombardment, leading to more compact films with increasing the bias voltage. On the other hand, the additional ion bombardment induces high stresses in the films. Stressed defects and strained bonds can increase the affinity for the etching agent. This material exhibits compact grain boundaries with lower etch potential [29] that causes the formation of etch features like the compact material, but etch at rates that are even higher than the RT material described by Kluth et al. The high compactness at the grain boundaries might be related to the improved texture.
3.5. Solar cells with IBAD-ZnO:Ga as front contact

Etched ZnO films that show suitable surface features were applied as front contacts in hydrogenated microcrystalline silicon solar cells (μc-Si:H). Therefore, the IBAD-ZnO:Ga films grown at a power of 100 W and 150 W at the ion source were reproduced and subsequently etched. Some drifts in the bias voltages are noticed for these samples compared to the films above (compare Table 1), which can be related to chamber coating owing to the sputtering process. To improve the optical properties, the film with \( U_{\text{Bias}} = 550 \) V was annealed in a vacuum chamber for 17 h at a temperature of 450°C after the etching process.

Table 2 itemizes the preparation conditions of IBAD-ZnO:Ga samples, the sheet resistance \( R_\square \) after etching in diluted HCl and the solar cell results. These are efficiency \( \eta \), fill factor \( FF \), open circuit voltage \( V_{\text{OC}} \), short circuit current density \( j_{\text{SC}} \), determined at \( j_{\text{SC}} \) and \( V_{\text{OC}} \) conditions of the μc-Si:H solar cells that were deposited on top of the ZnO:Ga films. Room temperature deposition and subsequent etching led to high sheet resistance values ranging from 27 \( \Omega_\square \) for \( U_{\text{Bias}} = 0 \) V to 85 \( \Omega_\square \) for \( U_{\text{Bias}} = 460 \) V and 60 \( \Omega_\square \) for 550 V, respectively. A remarkable decrease in \( FF \) from 65.6 % to 47.3 % was noticed, for IBAD-ZnO:Ga with \( U_{\text{Bias}} = 460 \) V, which resulted in a decrease of \( \eta \) from 4.1 % to 3.4 %. On the other hand, increasing \( U_{\text{Bias}} \) to 550 V led to improvement in \( FF \) to 66.0 % and a remarkable increase in \( \eta \) to 6.1 % is noticed. This improvement can be attributed to increased \( j_{\text{SC}} \), which increases with increasing \( U_{\text{Bias}} \) from 12.8 mA/cm\(^2\) to 17.7 mA/cm\(^2\) due to improved light trapping effect after texturizing the surface at high bias voltages (compare Figure 8).

Annealing at 450°C for 17 h in vacuum (base pressure of 7 \( \times \) 10\(^{-5}\) Pa) increases \( R_\square \) to 70 \( \Omega_\square \) by reduction of free charge carriers [30]. The post deposition annealing step increases especially \( j_{\text{SC}} \) to 20.7 cm\(^2\)/Vs mainly due to the higher transparency of the front contact (Figure 9 (a)). However, the cell efficiency suffers from lower \( FF \) and \( V_{\text{OC}} \).
The high $R_\infty$ of all IBAD-ZnO:Ga films limits the $FF$. The decrease in $FF$ can be ascribed to the increase in series resistance of the solar cells. Additionally, large deviation in the $V_{OC}$ was accompanied by low shunt resistance values, indicating that the design of the TCO-p-Si interface and absorber layer deposition might need further optimization on each type of the IBAD-ZnO:Ga surface.

Figure 9 (a) shows the total transmission of the RT grown ZnO:Ga and three IBAD-ZnO:Ga front contacts after etching. As already seen in Figure 6 an increase in transmission in the visible and in the infrared spectral range is clearly noticeable, when the films are grown by IBAD. IBAD-ZnO:Ga films show transmission values slightly above 77%. In contrary to Figure 6, the annealing process for the IBAD sample grown at $U_{Bias} = 550$ V did not show any increase in transmission in the wavelength range between 800 nm and 1100 nm. This can be attributed to internal light trapping effects due to the roughened surface. The high quality reference ZnO:Al usually exhibits transmission of more than 85% [31,32], the reduction in transmission can be related to absorption of defects in the band gap. These defects and free carrier density are responsible for the absorption of the light in the relevant spectral range. The deposition at $U_{Bias} = 550$ V improved the transmission slightly in the spectral range higher than 450 nm compared to the deposition at $U_{Bias} = 460$ V. Annealing at 450°C for 17 h in vacuum conditions led to additional improvement in the wavelength range especially below 450 nm. Figure 9 (b) displays the external quantum efficiency ($EQE$) and the integrated $j_{SC}$ values. Comparing the RT sample without ion bombardment, improvement in $EQE$ was achieved by ion beam assisted deposition in the whole spectral range, especially in the visible and in the short wavelength range. In correlation to the transmission curves improvement in $EQE$ was achieved by depositing IBAD-ZnO:Ga at a bias voltage of 550 V, especially in the spectral range between 400 nm and 800 nm. Subsequent annealing of this film showed further increase in $EQE$ in the spectral range between 350 nm and 550 nm as well as between 650 nm and 1100 nm. In correlation to Table 2 the calculated $j_{SC}$ values show increase with increasing $U_{Bias}$ from 14.2 mA/cm$^2$ for the unbombarded sample to 16.0 mA/cm$^2$ for IBAD-ZnO:Ga grown at $U_{Bias} = 460$ V, and 18.3 mA/cm$^2$ at $U_{Bias} = 550$ V, respectively. Subsequent annealing increases $j_{SC}$ to 20.5 mA/cm$^2$ due to improved transparency.

### Table 2. Bias voltages during deposition, Sheet resistances of etched IBAD-ZnO:Ga films with a size of 5 x 10 cm$^2$ and parameters of deposited μc-Si:H solar cells.

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<th>TCO</th>
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<th>$FF$ [%]</th>
<th>$V_{OC}$ [mV]</th>
<th>$j_{SC}$ [mA/cm$^2$]</th>
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4. Summary and Conclusion

Ion beam assisted deposition by using a ceramic ZnO:Ga target and an auxiliary ion source, which bombarded the films with \( \text{Ar}^+ \)-ions of an energy of few hundreds eV during deposition was successfully realized. The films were increasingly c-axis oriented, which is a hint that the crystalline order could be improved due to the IBAD technique for moderate ion energies. On the other hand, high compressive stress of \(-7.9\) GPa was observed and suggested to be responsible for the continuous decrease in the mobility from \(19.2\ \text{cm}^2/\text{Vs}\) to \(11.3\ \text{cm}^2/\text{Vs}\). The additional bombardment during growth led to a change in the microstructure, resulting in more compact films. However, the etching rate increased significantly with increasing bias voltage. The reason for this discrepancy can be attributed to increased stress due to the additional bombardment. Etch craters with a lateral size of up to \(600\ \text{nm}\) were revealed, which are usually achieved at higher growth temperatures, indicating that the film compactness increased due to the additional bombardment. Subsequent annealing in vacuum increased the transparency above \(77\%\) for the room temperature deposited films, and therefore the \(\text{EQE}\) showed improvement especially in the short and long wavelength range. This effect on ZnO:Ga material properties demonstrated a way to prepare texture-etched ZnO films for solar cell application by room temperature sputtering. These promising results open the route for low cost substrates like temperature sensitive plastic foils, the deposition onto devices or layer stacks.
5. Acknowledgements
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