ABSTRACT: A linear anode layer ion source was newly installed in a vertical in-line system. Argon and oxygen ions are generated to treat the HCl textured ZnO:Al films which are used as the transparent front contact in silicon thin film solar cells. The ion bombardment can modify the topography of the rough films which further give the chance to improve the current of the solar cells. The surfaces of the ZnO:Al films are eroded by the ions, and the etch rate is almost linearly proportional to the discharge power of the ion source. The resistivity of the treated films is not changed obviously by the argon ions. The textured ZnO:Al films are smoothened by the ion beam treatment, and the haze is slightly decreased. So far, microcrystalline silicon solar cells on the ion beam treated ZnO:Al films have lower efficiency and higher open-circuit voltage as compared to the untreated films. This might be caused by the fact that the silicon p-layer on treated ZnO:Al films have lower crystalline fraction.

Keywords: ZnO, Ion beam treatment

1 INTRODUCTION

Ion sources can be used for a wide range of applications such as surface activation, cleaning, etching, stress modification as well as ion implantation and various ion beam assisted deposition techniques [1]. Depending on the field of application, various ion sources are available which differ in terms of ion type, ion energy, ion energy distribution, ion current density and beam diameter. This contribution will present results on low energetic argon and oxygen ion beam treatment of aluminum doped zinc oxide (ZnO:Al) films on glass, which are commonly used as front contact electrode in silicon thin-film solar cells and modules [2].

High transparency, high conductivity and good light scattering are prerequisites of the front contact. The magnetron sputtered ZnO:Al film which is initially smooth fulfills the first two requirements. After etching in diluted hydrochloric acid (HCl), the films exhibit a surface texture which provides good light-trapping for the thin film solar cells. Low energetic argon and oxygen ion beam provides another choice to modify the ZnO:Al surface topography, which is important to the light scattering behavior of the solar cells.

The ion beam is generated from a linear anode layer ion source, which was newly installed in a vertical in-line reactor. Discharge voltage, discharge current, working pressure and source gas flow rate are the available parameters to characterize the working status of the ion source. The ion source can be switched between collimated mode and diffuse mode by varying source gas flow rate and working pressure. In the collimated beam mode, the discharge voltage is high, but the discharge current is low, and the ion beam is well collimated. In the diffuse mode, the ion source works with low discharge voltage and high discharge current, while the ion beam looks like a plasma cloud. In diffuse beam mode the cathode tends to be ionized. This results in a high concentration of iron ions in the ion beam, which leads to unintentional iron contamination of the substrate surface. Therefore, the work was relying on the collimated beam mode. In a collimated ion beam, the value of average ion energy in electron volt (eV) is approximately equal to \( \frac{1}{2} \) of the value of discharge voltage in volts (V) and the ion beam current is about 80-90% of the discharge current [3,4].

We characterized the dynamic etch rate of argon and oxygen ions on the ZnO:Al films, and compared the experimental results with the Transport of Ions in Matter (TRIM) simulation. The electrical, optical properties and the surface morphology of the ion beam treated ZnO:Al films were analyzed. Microcrystalline silicon solar cells were grown on the ion beam treated films, and we analyzed the Raman spectroscopy of the silicon layer.

2 EXPERIMENTAL DETAILS

All ZnO:Al films were prepared by rf magnetron sputtering on Corning glass substrates in an in-line sputtering system for a substrate size up to 30x30 cm² (VISS 300, supplied by von Ardenne Anlagentechnik GmbH, Dresden, Germany). The magnetron sputtered ZnO:Al films were then textured in diluted HCl acid. The textured ZnO:Al films were treated by argon or oxygen ion beam for different intensity and duration. The argon or oxygen ions, which are impinging on the zinc oxide surface – in our case under an angle of 40° towards the normal axis – lead to a subsequent removal of the thin films.

To ensure a uniform treatment, most films were etched in a dynamic process (the carrier moves in the vacuum chamber, perpendicular to the ion beam direction). The dynamic etching rate is defined as the following

\[
\text{DER} = \frac{d \times v}{s},
\]

where \( d \) is the removed thickness of the substrate, \( v \) is the speed of the carrier and \( s \) is the passes the carrier moves through the ion beam.

We investigated the dependence of the dynamic etch rate on the working gas pressure, argon gas flow, discharge voltage and discharge current and compare our results with TRIM simulations. TRIM calculates the stopping and range of ions in matter using a full quantum mechanical treatment of ion-atom collisions [5,6]. With TRIM program, sputtering yield (the number of substrate atoms leaving the substrate per incident ion) of argon and oxygen ions with different energies were simulated. By combining the sputtering yield and the discharge current, we calculated a static etch rate in nm/s.

The film thickness before and after treatment was measured by surface profiler (Dektak 3030 by Veeco...
Instruments Inc.) to identify the amount of removed materials. The electrical film properties were investigated by four-point probe. Optical transmission of the ZnO:Al coated glass was measured with a dual beam spectrometer (Perkin Elmer, Lambda 19). The resulting surface morphology was characterized by scanning electron microscopy (SEM) (LEO, Gemini). The roughness of the treated film was measured by atomic force microscopy (AFM). Microcrystalline silicon p-i-n solar cells were deposited on the ZnO:Al films by PECVD [7,8]. The silicon i-layer is 1.1 micrometer and the area of the cell is 1 cm$^2$. Solar cell characterization was performed with a Wacom solar simulator under standard test conditions (AM1.5, 100 mW/cm$^2$ and 25°C).

3 RESULTS AND DISCUSSION

3.1 Characterization of the ion beam

When the ion source works in collimated beam mode, the discharge voltage is controlled and the discharge current takes a certain value which depends on the discharge voltage, gas flow rate and working pressure. The discharge current is important because it is closely related to the ion beam current.

![Fig 1: Ion source discharge current as a function of gas flow rate at different discharge voltage. The dashed lines represent the maximum gas flow which the ion source could bear in collimated beam mode.](image1)

The values of the discharge current were taken by varying the discharge voltage, gas flow rate and working pressure, respectively. Fig 1 shows the function of discharge current versus argon gas flow rate for different discharge voltages at 2 microbar. There is a linear increase in the discharge current as more source gas is added to the system. At low discharge voltage, e.g. 0.5 kV, the discharge current only slightly increases with increasing flow rate. At high discharge voltage, the increase of discharge current is more pronounced. The end points of the data series represent the maximum operation gas flow in collimated beam mode. If the pressure overpasses the limitation, arcing will be ignited because of the high ionization of the gas atoms or molecules.

Further experiments show that the discharge current increases with increasing pressure. The working pressure in the chamber is determined by the butterfly valve of the molecular pump and the gas flow rate. The working pressure has a maximum operation limit in the collimated beam mode. If the pressure surpasses the limitation, arcing will be ignited because of the high ionization of the gas atoms or molecules.

3.2 Static and dynamic ion beam etching

The surface of ZnO:Al film is removed by the bombardment of ion beam. Fig 2 shows the removed thickness of a 32 cm wide substrate after 30 min static argon ion beam etching. We assume the ion energy distributions are similar at different positions, so the removed thickness is proportional to the ion beam current density, hence this figure shows the shape of the ion beam current density distribution. Clearly, the ion beam current density is not uniform, and it is much higher in front of the racetrack than in other areas. The difference between the two peaks is due to the fact that the ion source is 40 degree tilted. Because of the tilt, the distance between the left racetrack and the substrate is shorter than that of the right racetrack; therefore in the figure the left peak is higher than the right one. The static etch rate is calculated as

$$\text{SER} = \frac{d}{s},$$

where $d$ is the removed thickness (here we take the left peak), $s$ is the treatment time.

![Fig 2: Removed thickness of a 32cm-wide ZnO:Al substrate when the ion source is 40° tilted and works in collimated-beam mode.](image2)

Fig 3 shows the dependency of dynamic etch rate on the Ar gas flow rate for two pressures at fixed discharge voltage of 1 kV. The blue squares are the etch rates of 1 microbar. The etch rate increases linearly with increasing gas flow. The black circles are the etch rates at 2 microbar. The trends are similar, but the etch rates are higher, which is due to the higher discharge current at higher pressure. The empty circles are the discharge current at 2 microbar (these data points are taken from Fig 1). With higher gas flow, the discharge current increases, so does the etch rate and the trend of increasing etch rate is similar to that of current increasing. Further experiments show that the dynamic etch rate increases with increasing discharge voltage.
Fig 3: Dynamic etch rate as a function of argon gas flow rate at different working pressure.

Fig 4: Dynamic etch rate as a function of ion source power for Ar and O₂ ion beam. The lines are the guides to the eye.

The dynamic etch rate as a function of the ion source power (the product of discharge voltage and discharge current) for argon and oxygen ion beam is plotted in Fig 4. The etch rate of oxygen ion beam is lower than that of the argon ion beam, which is caused by the difference between the mass and may also be the different relation between ion and discharge current of argon and oxygen ions. For both ion beams, the etch rate shows almost linear dependency on the ion source power, independent from the gas flow rate and the pressure. The relationship between etch rate and ion source power may be explained by the physical principle of the collision between the impinging ions and substrate. The average ion energy, which is proportional to the discharge voltage, determines how many substrate atoms per incident ion leave the sample surface. In collimated beam mode, the ion beam current, which means the number of ions per second in the ion beam, is proportional to the discharge current. Ion energy and ion beam current are two decisive parameters to the amount of sputtered substrate atoms, so that the etch rate has the linear dependency of the ion source power.

The etch rates simulated by the TRIM program are shown in Fig 5 (the empty circles). To compare with the experimental results, the dynamic etch rate data were transferred to the equivalent static etch rate. To find out the factor between the dynamic etch rate and the static etch rate, several treatments with same etching parameters were done with static carrier and dynamic carrier, respectively. We found for the tilted ion source (40°), $DER = SER \times 0.1 \ m$. The dynamic etch rates in Fig 4 were transferred to the equivalent static etch rates (The solid circles in Fig 5). Fig 5 shows that the experimental results fit to the simulation very well.

Fig 5: Comparison of simulated and experimental etch rate for argon and oxygen ion beam. The lines are the guides to the eye.

3.3 Electrical properties, optical properties and surface morphology of ion beam treated ZnO:Al films

The ion beam etching not only erode the ZnO:Al films, but also changes its topography. Fig 6 shows the SEM images of argon ion beam treated ZnO:Al films, in which the left one is without treatment, and from the left to the right, the treatment time is increasing. One can see that the boundaries of the craters are smoothened while ZnO:Al material is etched away, and the craters show orientation after long time ion beam etching because of the direction of the impinging ions. In these images, ions come from the left direction.

Fig 6: SEM images of Argon ion beam treated ZnO:Al films.

The removed thickness and roughness according to the etching time of these films are plotted in Fig 7. The removed thicknesses are increasing linearly with the etching time, which means that the etch rate is stable during the etching process as long as the etching parameters keep the same. The roughness of the films decreases with etching time. Thus, the ion beam treatment has a smoothening effect on the ZnO:Al films.

The thinned-down films exhibit a higher sheet resistance due to the reduction of the thickness. However, the resistivity remains almost constant. The haze of the ZnO:Al film is slightly decreased by the ion beam treatment.
3.4 Solar cells

Table 1:

<table>
<thead>
<tr>
<th>Substrate</th>
<th>( \eta )</th>
<th>FF</th>
<th>( V_{oc} )</th>
<th>( J_{sc} )</th>
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</thead>
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<td>Reference</td>
<td>7.45</td>
<td>72.7</td>
<td>499</td>
<td>20.5</td>
</tr>
<tr>
<td>Ion treated</td>
<td>7.33</td>
<td>72.6</td>
<td>503</td>
<td>20.1</td>
</tr>
</tbody>
</table>

Fig 8 The quantum efficiency of solar cell based on the ion beam treated ZnO:Al film.

Microcrystalline silicon p-i-n solar cells were prepared on the reference and ion beam treated ZnO:Al films. The ZnO:Al film was treated by the argon ion beam for one minute. The removed thickness is around 12 nm. The change of the surface morphology is so little that it can not be observed by SEM or AFM. The solar cell results (Table 1) show that the short-circuit current density is slightly decreased and the open-circuit voltage is slightly increased. Fig 8 shows that the quantum efficiency in the short wavelength region is decreased. Raman spectroscopy experiments show that the silicon p-layer has a lower crystalline fraction on the ion beam treated ZnO:Al film. This may be a cause for the reduced blue response and higher \( V_{oc} \) of the solar cell. Improvements of fill factor (FF) and open circuit voltage (\( V_{oc} \)) by plasma treating on LPCVD ZnO films have been reported [11]. This might also be explained by an altered p-layer. Further experiments to improve the crystalline fraction of silicon p-layer via varying the silicon growth deposition parameters are expected.

4 CONCLUSIONS

The linear anode layer ion source is characterized with argon and oxygen as source gas. The etch rate of magnetron sputtered ZnO:Al films by argon and oxygen ion beam is almost linear depending on the product of discharge voltage and discharge current, in which the latter is adjustable by the amount of source gas and the working pressure. The etch rates are in good agreement with TRIM simulation. Argon ion beam etching could smoothen the texture structure of the HCl etched ZnO:Al films, without influencing the electrical properties. Thin film solar cells based on the ion beam treated ZnO:Al films show decreased quantum efficiency in the blue light region, which might be caused by the lower crystalline fraction of silicon p-layer on the ion beam treated ZnO:Al films. Adjustment of the crystalline fraction of silicon on ion beam treated ZnO:Al films are planed.

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REFERENCE