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AZO layers deposited by PLD method as flexible transparent emitter electrodes for solar cells

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ABSTRACT

The paper presents investigation of aluminum doped zinc oxide (ZnO:Al or AZO) layers in terms of their application as transparent front contacts in flexible photovoltaic cells. Studied ZnO:Al thin films were deposited, for the first time, by using pulsed laser deposition technique (PLD) on PET foil. The essential parameters of obtained AZO transparent conductive layers (TCL), such as optical transmission, resistance per square and mechanical durability, were measured and analyzed. Additionally the composition and structure of manufactured layers were tested by HRSEM, EDX and XRD methods. Direct connections between the beam wavelength, AZO structure and obtained TCO layer were revealed.

1. Introduction

Transparent emitter electrodes for flexible solar cell applications determine one of the key challenges in new generation photovoltaic technology. Thin film photovoltaic cells need transparent window (emitter) electrodes for light transmission, as well as for extraction of the photocurrent. Such layers should meet the compromise between the highest possible optical transmission (at least 80% for visible spectrum) and the lowest sheet resistance [1]. Moreover, the structure must be bending resistant and its electrical parameters should be sufficiently stable under the influence of mechanical stresses [2]. Materials, commonly used for that purpose are ITO, FTO, Zn_2SnO_4, Cd_2SnO_4, AZO [3–5], CdO, ZnO or $RuSiO_4$ [6]. Also TiO_2 and carbon nanostructure layers are under investigation [7].

It has been well known that ITO is the most commonly used TCO, because of its low resistivity and high optical transmittance [8]. However, its chemical instability, toxic nature [9] and high cost, combined with its bending irresistance [8], have stimulated efforts to find an alternative TCO material for emitter electrode, especially concerning flexible solar cells applications.

Amongst approachable materials, aluminum doped zinc oxide (ZnO:Al or AZO) is one of the most attractive solution. It is caused due to low cost of ZnO, its high abundance on Earth, low toxicity and low film resistivity [10]. ZnO also benefits from a higher absorption coefficient than other wide bandgap materials, as well as easy fabrication methods, which results in lower manufacturing costs of ZnO-based devices. ZnO is typically crystallized in the hexagonal wurtzite structure with possibility of attaining high carrier concentration by the proper material doping [11].

In order to achieve low resistivity, required for the application of ZnO thin films as transparent conductive layers, two different methods can be applied [12]:

- creation of intrinsic donors by lattice defects (e.g. oxygen vacancies or zinc atoms on interstitial lattice sites);
- introduction of extrinsic dopants (metals with oxidation number three on substitutional metal lattice sites or halogens with oxidation number minus one on oxygen lattice sites).

The first method can be realized during the deposition, by carefully adjusting oxygen partial pressure and deposition rate. The other way is a reduction process of the oxide film after deposition, e.g. by annealing in vacuum or in a hydrogen containing atmosphere [13]. However, it has been found that such intrinsically doped zinc oxide films are not characterized with application acceptable properties. Primary, the resistivity value is in the range of 10^{-2} to 10^{-3} Ωcm, which is too high for using as TCO. Furthermore, these films are not stable at ambient conditions (mainly at higher temperatures), which is caused due to the reoxidation of the oxygen deficient or zinc rich films, which significantly increases its resistivity [14].

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The second method allows to achieve resistivity as low as 2×10^{-4} Ωcm, through high doping levels with carrier concentrations up to 1.5×10^{21} cm^{-3}, by addition of trivalent dopants, B, Al, Ga, In. The research shows that different dopants lead to nearly the same resistivities, however, aluminum is the dopant mostly used, followed by gallium and boron [15]. Authors of this paper concentrated on Al doped ZnO, due to its potentially the most attractive performance.

2. ZnO:Al film deposition method

In order to obtain appropriately high optical transmittance combined with low resistivity, AZO layers are usually deposited using relatively complicated techniques, such as magnetron sputtering [16] or modified CVD methods [17,18]. All deposition methods yield resistivities below 10^{-3} Ωcm. However, the plasma assisted processes, such as magnetron sputtering and pulsed laser deposition (PLD), lead to the lowest resistivities for ZnO:Al films. This is caused by the fact that these methods rely not only on thermal activation of the growth process, but also benefit from the additional energy input from energetic particles (ions, sputtered atoms, energetic neutrals). These methods can be used to prepare films of better crystalline and electronic quality, as well as to deposit films at lower substrate temperatures. Additionally, pulsed-laser deposition is a very versatile technique, which can be used for material screening and for the determination of the intrinsic material data [15].

Due to its favorable properties, authors propose to utilize AZO thin layers obtained by the new, experimental pulsed laser deposition method as transparent conductive layer for flexible PV electrode application. This method is one of the laser techniques, widely used in photovoltaic technology [19–21], unique by high kinetic energy of produced molecules. Using this technique highly stohiometric layers with the resistivity as low as 0.85×10^{-4} Ωcm are possible to be produced [22]. By adjusting of process parameters authors are planning to manufacture flexible, transparent and conductive TCO layer on inexpensive, low-temperature polymer foil.

The PLD technique uses high power laser pulses to melt, evaporate and ionize material from the surface of a target. The vaporized material, containing neutrons, ions, electrons etc., is known as a laser-produced plasma plume and expands rapidly away from the target surface. Film growth occurs on a substrate upon which some of the plume material recondenses. However, in practice the situation is not so effortless, with a large number of variables affecting the properties of the film, such as laser fluency, background gas pressure and substrate temperature. These variables allow the film properties to be manipulated in order to suit individual applications. Nevertheless, such optimization requires a considerable effort. Indeed, much of the early research into PLD was concentrated on the empirical optimization of deposition conditions for individual materials and applications, without attempting to understand the processes occurring as the material is transported from target to substrate.

The technique of PLD has significant benefits over other film deposition methods, such as:

- the capability for stoichiometric transfer of material from target to substrate,
- relatively high deposition rates (this can be achieved at moderate laser fluencies, with film thickness controlled in real time by simply turning the laser on and off),
- high process purity due to the fact that laser is used as an external energy source (thus, deposition can occur in both inert and reactive background gases),
- the possibility of deposition multilayer films without breaking the vacuum (due to the use of a carousel, housing a number of target materials).

Proposed, experimental PLD system consists of a vacuum chamber equipped with turbo molecular pump and Nd:YAG laser with fourth harmonic generation module and pulse length of 26 ns. The schematic setup of the system is presented in Fig. 1.

Pulsed laser beam, directed by the mirror system (Fig. 1-3), was focused on the surface of the target (Fig. 1-5) by quartz long focal-length lens (Fig. 1-4). To avoid crater effect on the surface, target was constantly rotated and the evaporated material was subsequently deposited on the substrate. For adhesion improvement substrates were placed on heated base (Fig. 1-6). Inner pressure and gas content were controlled by the system (Fig. 1-1) and a valve (Fig. 1-2) [24]. Material of the target was acquired by pressing of 98% ZnO and 2% Al_2O_3 powders. By this method it was possible to create relatively uniform ZnO:Al layers with thicknesses of 90–100 nm. Five series of samples with the following parameters were prepared:

- D1-P3-1 – beam wavelength 355 nm, oxygen pressure 1.2×10^{-2} mbar
- D2-P2-1 – beam wavelength 266 nm, oxygen pressure 1.2×10^{-3} mbar
- D2-P3-1 – beam wavelength 266 nm, oxygen pressure 1.2×10^{-2} mbar
- D2-P3-2 – beam wavelength 266 nm, oxygen pressure 1.2×10^{-2} mbar
- D2-P3-3 – beam wavelength 266 nm, oxygen pressure 1.2×10^{-2} mbar

3. Experimental ZnO:Al layers on flexible substrates

As a result, continuous, smooth layer of the ZnO:Al was obtained. Fig. 2 presents examples of deposited ZnO:Al layer on flexible substrates of PET foil (a) and Kapton® foil (b) substrate.

The quality of each sample was tested by HRSEM microscopy, which is shown in Fig. 3. Strongest crystallization was observed in case of PET/D1/P3/1 sample (Fig. 3b). By EDX analysis expected composition of manufactured layer was confirmed. As the additional impurities Cl and S were detected.

Deposited samples were characterized in terms of their optical transmission and electrical resistance. Optical transmission curves of ZnO:Al layers in visible spectrum (Fig. 4) were determined by optoelectronic setup with silicon photo detector and stabilized light source. Obtained optical transmission is sufficiently high, at the average level of 90%.

The next step was a verification of electrical and mechanical properties of deposited layers. Resistance per square was measured for each sample before and after a series of dynamic bending cycles, using 4-probe measuring setup, according to A-De Matti method. The procedure of bending was realized using 25 mm diameter cylinder with movement frequency of 3 cycles per second. The results of resistance changes after 200 bending cycles are shown in Table 1.

4. Conclusions and further development

Comparing to results previously reported by authors [23], significant improvement of optical, and electrical parameters, by PLD procedure enhancement was achieved. According to the results (Fig. 4), it should be noted that there is an optimal pressure inside the chamber corresponding with an appropriate wavelength of the beam, which influences the highest optical transmission and