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Property control of expanding thermal plasma deposited textured zinc oxide with focus on thin film solar cell applications

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Abstract

Property control of expanding thermal plasma deposited textured zinc oxide is demonstrated considering intrinsic, i.e. bulk, and extrinsic transparent conducting oxide quality relevant for application in thin film amorphous silicon pin solar cells. Particularly the interdependence of electrical conductivity, film composition and film morphology, i.e. structure, feature shape and roughness of the surface, is addressed. Control of film composition is mainly governed by plasma production and gas phase chemistry inherently inducing a significant contribution to film morphology, whereas control of film morphology solely is governed by near-substrate conditions. Especially the ratio of zinc to oxygen and the reactor chamber pressure appear to be determinative in obtaining zinc oxide exhibiting the appropriate intrinsic and extrinsic quality, i.e. a high electrical conductivity, a high transmittance, a textured rough surface morphology and a strong hydrogen plasma resistance. The solar cell performance of appropriate undoped and aluminium doped textured zinc oxide inherently obtained during deposition is comparable with respect to Asahi U-type fluorine-doped tin oxide.

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1. Introduction

Owing to unique combined electrical and optical properties, transparent conducting oxides have found a wide variety of applications like thin film solar cells, architectural glazing, display devices, electro chromic devices, and gas sensors [1]. Each application sets different demands on the materials properties. An appropriate measure of the performance of a transparent conducting oxide reflecting its intrinsic bulk quality is the ratio of the electrical conductivity σ to the visible absorption coefficient α. The quantity σ/α is a Figure of Merit for rating transparent conducting oxides [2], the larger the value of this quantity, the better the performance of the transparent conducting oxide is. The Figure of Merit generally increases with film thickness, as the intrinsic transparent conducting oxide quality depends on e.g. average crystallite size. Besides intrinsic quality, generally also specific extrinsic quality is required like e.g. mechanical, chemical and thermal durability, surface morphology, and etchability. Extrinsic quality of particular relevance for application as a front contact in thin film amorphous silicon pin solar cells includes an appropriate textured rough surface morphology for effective light trapping and a strong hydrogen plasma resistance [3]. Deposition temperature, cost and environmental impact are other factors that may influence the choice of transparent conducting oxide for any particular application.

Zinc oxide (ZnO) is a transparent conducting oxide of considerable technological interest for application in amongst others silicon based thin film solar cells [4]. It exhibits superior transparency, stronger resistance to hydrogen plasma and allows for lower deposition temperature,

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lower cost and less environmental impact as compared to the commonly used fluorine-doped tin oxide (SnO_2:F) [5,6]. The latter is preferred in thin film solar cells since it has an excellent pyramid-like surface texture enabling effective light trapping properties. Textured ZnO films have been prepared by several deposition techniques [7–10] and post deposition wet chemical etching of smooth films [11]. Recently, the utilization of expanding thermal argon plasma created with a cascaded arc is successfully demonstrated for low temperature deposition of textured ZnO [12].

The electrical conductivity of ZnO is directly related to the charge carrier density and mobility. Whereas the charge carrier density is determined by intrinsic or extrinsic donors present, the mobility mainly depends on the mechanism by which the carriers are scattered by lattice imperfections, e.g. ionised impurity scattering and grain boundary scattering [1]. The electrical conductivity thus depends on both composition and morphology of the transparent conducting oxide, which in turn depend on the deposition parameters. Separate control of film composition, i.e. carrier density, and film morphology, i.e. carrier mobility, is highly desirable. Presumably control of film composition will be governed by plasma production and gas phase chemistry, i.e. chemically induced effects, whereas control of film morphology will be particularly determined by near-substrate conditions, i.e. physically induced effects. Both the ratio and nature of particular reactive species arriving at the substrate surface as well as the arrival rate and surface mobility of these species arriving at the substrate surface need to be considered.

In this article, the property control of expanding thermal plasma (ETP) deposited textured ZnO is addressed particularly considering the interdependence of electrical conductivity, composition and morphology. As an example, suitability for application as a front contact in thin film amorphous silicon pin solar cells will be demonstrated. This requires a transparent conducting oxide exhibiting the appropriate intrinsic and extrinsic quality.

2. Experimental details

Undoped and aluminum doped ZnO films are deposited on Corning 1737F glass substrates utilizing an expanding thermal argon plasma created by a cascaded arc as described in detail elsewhere [12]. The plasma source is a wall-stabilised cascaded arc consisting of three cathodes, a stack of circular copper plates insulated from each other by boron nitride rings and a grounded anode plate. The plasma emanates from the cascaded arc through a nozzle, expands supersonically into a low-pressure reactor chamber (20–250 Pa), shocks, and flows at subsonic velocity towards a substrate. Precursors are oxygen, diethyl zinc and additionally for doped films trimethyl aluminium (TMA). The liquid precursors are supplied to the reactor chamber utilizing conventional mass flow controllers and pressure-controlled bubblers using argon (purity grade 5.0) as a carrier gas or Bronkhorst Hi-Tec Controlled Evaporation and Mixing systems. With the latter the precursor feed rate is controlled in its natural liquid state at ambient conditions using a liquid mass flow metre and subsequently evaporated in a continuous way with the aid of argon (purity grade 5.0) as a carrier gas [13]. A summary of the deposition conditions explored is shown in Table 1, no post-deposition treatment is performed.

The remote configuration of the expanding thermal plasma technique allows for separate adjustment of plasma production (e.g. arc argon flow), gas phase chemistry (e.g. oxygen flow, trimethyl aluminium flow) and near-substrate conditions (e.g. reactor chamber pressure, temperature) [14], independently affecting intrinsic and relevant extrinsic transparent conducting oxide quality. As opposed to direct plasmas, the substrate holder or electrode does not play a role in plasma production implying the absence of any significant ion bombardment [15,16] and ultraviolet light exposure.

Film thickness and sheet resistance are determined with a Tencor P-10 step profiler and a van der Pauw 4-point probe, respectively. All presented films have comparable thickness values around 1200 ± 50 nm to be suitable for application in thin film amorphous silicon pin solar cells.

A Phystech RH 2010 Hall Effect Measurement System is used to determine sheet resistance, carrier density and carrier mobility for a limited number of films. In order to visualise film morphology, a JEOL JSM-6330 F Field Emission Scanning Electron Microscope (SEM) operated at 5.0 kV is used. X-ray diffractograms (XRD) were recorded with a Philips X-pert SR 5068 powder diffractometer equipped with a Cu Kα source to determine film structure. Root mean square roughness is analysed with a Park Scientific Instruments Autoprobe CP 100μm Atomic Force Microscope operated in contact mode employing sharpened nitride, gold coated microlevers. Total and specular transmittance is measured using a Perkin Elmer Lambda Ultraviolet/Visible/Near Infrared double beam spectrophotometer equipped with integrating sphere. Spectrally resolved haze values are determined as the ratio of diffuse to total transmittance, i.e. the ratio of light that is scattered compared to the total intensity of light at the interface. Amorphous silicon pin solar cells were deposited simultaneously on ETP deposited ZnO and Asahi U-type SnO_2:F as a reference by Radio Frequency (RF) and very high frequency Plasma Enhanced Chemical Vapour Deposition

Table 1
ETP deposition conditions explored in relation to ZnO quality

Substrate temperature	423–573 K
Oxygen flow	50–120 sccm
Diethyl zinc flow	5.15 sccm
Trimethyl aluminium flow	0–0.481 sccm
Arc argon flow	800–1400 sccm
Arc power	3.1 kW
Reactor chamber pressure	20–250 Pa