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Plasma treatment for crystallization of amorphous thin films

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Abstract

The crystallization of amorphous metal oxide thin films was achieved by RF plasma treatment. Although various amorphous films are crystallized after 2 min or so, the sample temperature is lower than 150 °C without compulsory cooling even when the films are treated for 1 h. The oxygen gas pressure on the plasma treatment was found to be the key parameter on the crystallization. This treatment works on amorphous films of various materials, independently of the film preparation method and substrate materials.

Keywords: Crystallization; Plasma processing; Titanium oxide; Indium oxide; X-ray diffraction

1. Introduction

In recent times, functional coatings have been expanding its application area widely, and the materials have been becoming deposited on various substrate: conventionally on silicon wafers and glass sheets and currently on plastic films for flexible displays application, for example. However, plastic materials have a poor heat resistance in general, and crystalline films are, therefore, difficult to be deposited on them.

Annealing by laser scan has been applied to amorphous silicon films deposited on plastic sheet substrates for TFT circuit construction in flexible displays [1] but the line-scanning method has a poor productivity problem intrinsically. Microwave treatment might be one candidate for densification/crystallization process with a high productivity but it is being used as a thermal sintering method for bulk ceramic powder cast yet [2,3]. Such thermal processes are not desirable because plastic substrates have more than 10 times of thermal expansion coefficient (50–70 ppm/°C) than that of glass substrate (ca. 5 ppm/°C), which difference should be one cause of the problems in fine pattered devices [4].

PVD (physical vapor deposition) technology is still a mainstream production tool for functional coatings. On the other hand, printing technology of sol–gel solutions shows a tremendous progress and now is the most promising technology as a highly productive process in a wide array of applications also for optical stack devices [5]; still, for its real adaptation to the production, the most desired is also the sophisticated densification/crystallization technology.

We have developed a crystallization technology using RF plasma. Various amorphous metal oxide films were successfully crystallized and densified by less than 5-min treatment without severe rise in film temperature.

2. Experimental

Amorphous ITO films were deposited by DC sputtering method on soda–lime glass and PET films with 15-nm-thick SiO_2 alkali-barrier layer with using an inline-type magnetron sputter coater (Shinku Seiko Ltd., SP-D-3). The sputter machine has a deposition chamber with a load lock and over run chambers on both ends. The deposition chamber is divided into three chambers with one cathode in each chamber. The sputter gas is introduced into each deposition chamber and evacuated through the end chambers with two diffusion pumps. ITO was deposited using a ceramics target having a 90 wt.% In_2O_3–10 wt.% SnO_2 composition, and a sputter gas of 3% O_2 diluted with Ar and a DC power supply (Advanced Energy Inc., MDX) was used. The substrate

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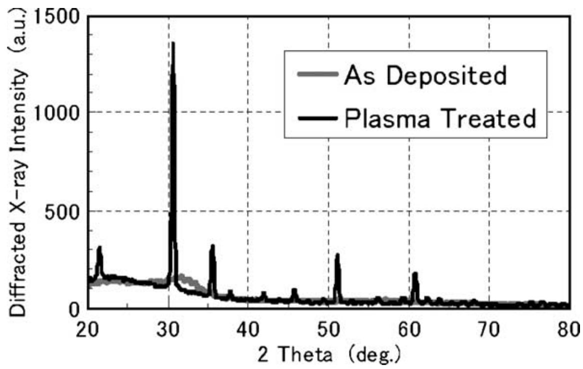

Fig. 1. X-ray diffraction profiles of ITO film before and after plasma treatment.

temperature does not exceed ca. 30 °C, and amorphous ITO films were obtained. Alkali-barrier SiO_2 was deposited from a quartz target in an Ar-based sputter gas including 5% O_2 with using a solid-state 13.56 MHz RF power generator (ENI Technology, Inc., OEM-12A) and an auto-impedance matcher (ENI Technology, Inc.).

Amorphous TiO_2 films were prepared by spin-coating method with a commercial titanium alkoxide solution (Nihon Soda Ltd., NDH-510C) on ⟨100⟩ Si wafers. Si wafer substrate with 4 in. diameter and 0.5 mm thickness was chemically etched before the deposition. After the coating and drying in a clean oven, the samples were irradiated with UV light and amorphous TiO_2 films were obtained.

The films were treated with capacitively coupled RF plasma in a barrel-type chamber having a pair of electrodes covering the half part of the cylinder wall with each; the details of the plasma-treatment conditions will be described elesewhere because of its patent situation. Alkoxide-derived TiO_2 film on Si wafer was heated at 500 °C in air for 1 h in order to compare its crystallinity and packing density with those of the plasma-treated TiO_2 films.

The thickness of the films was measured using a stylus-type surface tracer (Veeco Instruments Inc., Dektak) and a laser profile microscope (Keyence Co, Ltd., VK-7510). Sheet resistance of the ITO films was measured with a collinear four-point probe (Mitsubishi Chemical Corp., Loresta MCP-T600). The crystalline structure of the films

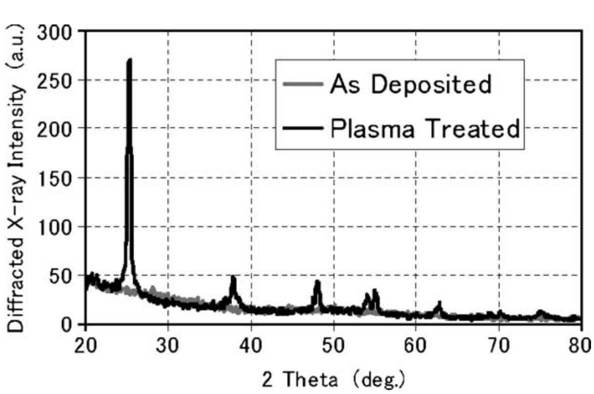

Fig. 2. X-ray diffraction profiles of 270-nm-thick TiO_2 film before and after plasma treatment.

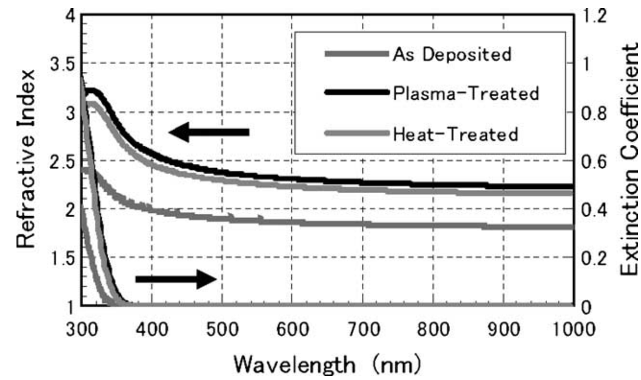

Fig. 3. Optical constants of 279-nm-thick as-deposited, plasma-treated and heat-treated TiO_2 films.

was evaluated by asymmetric XRD method employed Seemann–Bohlin arrangement with a fixed X-ray incident angle of 0.8°. Refractive index of TiO_2 films was analyzed based on the parametric semiconductor model using ellipsometric data (psi and delta) obtained from a spectroscopic ellipsometer (J.A. Woollam Co., Inc., VASE) and transmittance data measured by a grating-type spectrometer (Perkin Elmer Inc., LAMBDA900).

3. Results and discussion

The XRD rocking curves of the 150-nm-thick ITO film on soda-lime glass substrate with 15-nm-thick silica alkali-barrier are presented in Fig. 1. The figure shows that 5-min plasma treatment is quite effective to crystallize the ITO film and the crystallized ITO is found to have a bixbite structure. While the plasma treatment condition was not well adjusted, the sheet resistance of the ITO films decreased 10% more by this plasma treatment.

Amorphous sputtered ITO on PET with 15-nm-thick SiO_2 gas-barrier layer was crystallized for 5-min plasma treatment and no damage on PET substrate was observed. Also, its electric resistivity decreased by the treatment.

It is well known that TiO_2 is a material which is much difficult to crystallize than ITO and generally needs nearly

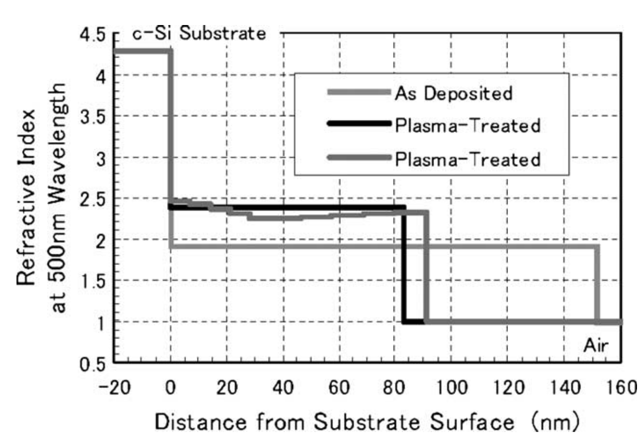

Fig. 4. Depth profile of refractive index at 500 nm wavelength.