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Room temperature crystallization by RF plasma

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Abstract

The crystallization of amorphous thin films was achieved by radiofrequency (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. This treatment works on amorphous films of various materials, independently of the film preparation method and substrate materials. Sol–gel-derived TiO_2 films were densified and simultaneously crystallized to anatase structure by the plasma treatment and the obtained films indicate almost the same photocatalytic activities as that of thermally crystallized TiO_2 films. Plasma-crystallized sputtered indium tin oxide (ITO) films have a bixbite structure and the resistivity reached to 1.6×10^{-4} Ω cm while the crystallization condition was not optimized. Amorphous silicon films with a small mount of crystallites were deposited by sputtering method and were crystallized by the plasma treatment.
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Keywords: Crystallization; Plasma processing; Titanium oxide; Indium oxide; X-ray diffraction; Photocatalysis; Amorphous silicon

1. Introduction

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

Laser-induced melt–regrowth method has been applied to amorphous silicon films deposited on plastic sheet substrates for thin film transistor (TFT) circuit construction in flexible displays [1] but the laser-scanning method has intrinsic problems such as poor uniformity and less productivity over large-area application. Microwave treatment might be one candidate for densification/crystallization process but it is still a thermal sintering method for bulk ceramic powder cast [2,3]. Such thermal processes are not desirable because plastic substrates have more than ten times larger thermal expansion coefficient (50–70 ppm/°C) than that of glass substrate (ca. 5 ppm/°C), a difference which is one cause of the problems in fine-patterned devices [4].

Physical vapor deposition (PVD) technology is still a mainstream production tool for functional coatings; however, fine-patterned coating is obtained through photo-lithographic processes which are time-consuming and expensive. On the other hand, printing technology has been highlighted in the research stage because it is now the most promising, having a highly productive process in a wide array of applications also for electronic circuits, optical stack devices, biodevices, and so on. Nano imprinting technology [5,6] is a room-temperature process for obtaining fine-patterned coatings and has also derived the web-printing technology [7]. However, nano printing technology can only coat organic polymer films and this material restriction is still a problem for realizing a wide variety of functional devices.

Sol–gel technology can synthesize various inorganic materials and printing technology of sol–gel solutions shows tremendous progress [8]; still, for its real adaption to the production, the most desired is the sophisticated densification/crystallization technology.

We have developed a crystallization technology using RF plasma. Various amorphous films were successfully crystallized and densified by a less-than-5-min treatment without severe rise in film temperature. In this paper, we will discuss plasma crystallization of sol–gel-derived TiO_2 films, sputtered ITO films and sputtered silicon films.

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2. Experimental

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

Amorphous ITO films were deposited by direct current (DC) sputtering method on soda–lime glass with 15-nm-thick SiO_2 alkali barrier layer 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 overrun 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 in Ar and a DC power supply (Advanced Energy Inc., MDX) was used. The substrate temperature does not exceed ca. 30 °C during the deposition process 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 using a solid state 13.56 MHz RF power generator (ENI Technology, Inc., OEM-12A) and an auto impedance matcher (ENI Technology, Inc.).

Amorphous silicon films with a small amount of crystallites were deposited on soda–lime glass substrate by pulse-modulated DC sputter method using a pulsed DC plasma generator (ENI, RPG-50). The sputter target used is a Si polycrystalline with a ca. 1×10^{-3} Ω cm resistivity and Ar including 5% H_2 was used as a sputter gas.

Films were treated with capacitively coupled RF plasma in a barrel-type chamber having a pair of electrodes covering the each half part of the cylinder wall with each electrode; details of the plasma treatment conditions will be described elsewhere because of the patent situation. The film temperature during the plasma treatment was measured by using a radiation thermometer and its reproducibility was about ±4 °C. The 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 photocatalytic activities with those of the plasma-treated TiO_2 films.

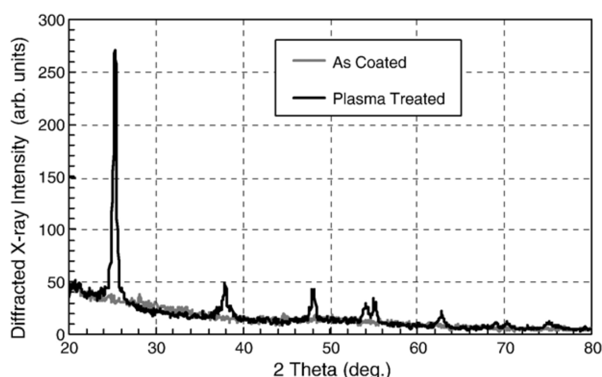

Fig. 1. X-ray diffraction profiles of 270-nm-thick TiO_2 film before and after plasma treatment.

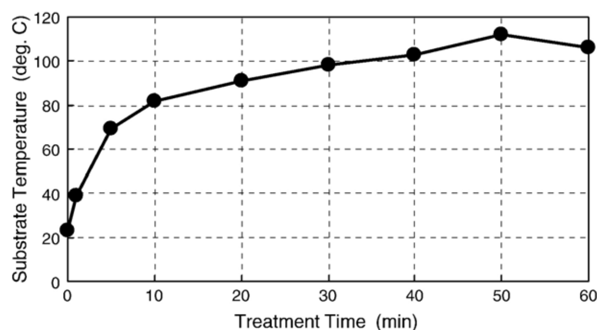

Fig. 2. Substrate temperature during the plasma treatment.

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). The crystalline structure of the films was evaluated by asymmetric XRD (X-ray Diffraction) method employing Seemann–Bohlin arrangement with a fixed angle between X-ray incident beam and film surface being 0.8° for TiO_2 and ITO or 0.25° for silicon.

Photocatalytic efficiency was evaluated by the degradation of gaseous isopropanol (IPA) under 1.0 mW/cm^2 UV light irradiation (Toshiba Lighting & Technology Co., Black light bulb BLB); the film sample was placed in a 1000-ml Pyrex vessel and the initial IPA concentration was set about 1000 ppm. The UV intensity was measured using a UV power meter (TOPCON Co., UVR-2). Concentrations of IPA and acetone which is a reaction intermediate from IPA to CO_2 and H_2O, were measured using a gas chromatograph (Shimadzu Co., GC-8A) equipped with a 5-m PEG1000 column and a flame ionization detector using N_2 carrier gas. CO_2 concentration was measured by using the same GC-8A with a 2-m active carbon column and a methanizer and a flame ionization detector using N_2 as a carrier gas. The photo-degradation rate is evaluated from the decreasing rate of IPA concentration in the very early period of the UV irradiation in order to eliminate the rate-determining contribution of the IPA adsorption onto the sample surface. Surface wettability was evaluated by the water contact angle following the sessile drop method using a contact angle meter (Kyowa Interface Science Co., Ltd., CA-X).

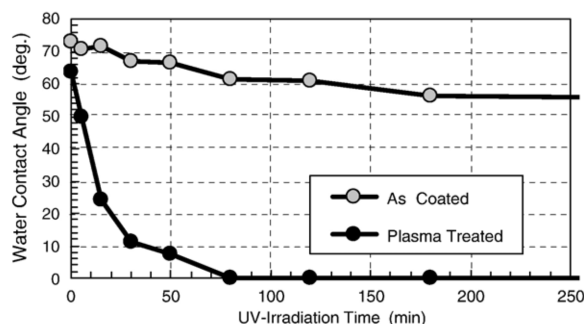

Fig. 3. Contact angle change of a water droplet placed on TiO_2 films with and without plasma treatment by UV-light irradiation.

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