Thin Solid Films 517 (2009) 3092–3095

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Room-temperature crystallization of amorphous films by RF plasma treatment

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ARTICLE INFO

Available online 20 November 2008

Keywords:
Crystallization
Plasma processing
Radio frequency
Indium oxide
Titanium oxide
Amorphous silicon

ABSTRACT

The crystallization of amorphous thin films was achieved by 13.56 MHz RF (radio frequency) plasma treatment. This crystallization process has a strong advantage that the sample temperature is lower than 120 °C during the plasma treatment even without compulsory cooling and various amorphous films are crystallized after 2 min or so. This treatment works on amorphous films of various materials, independently of the film preparation method and substrate materials. Crystallization has been confirmed on amorphous thin films of sputtered ITO (tin doped indium oxide) deposited on soda-lime glass and PET (polyethylene terephthalate), of sputtered TiO_2 on soda-lime glass, of sol–gel derived TiO_2 on silicon wafer and of sputtered hydrogen-doped silicon on soda-lime glass.

The plasma gas pressure was found to be the key parameter in the plasma crystallization process. The appropriate gas pressure depends on the plasma gas species and not on film or substrate materials. A Cu electrode, attached to the backside of the substrate and is electrically floated from the electric ground, was found to enhance the plasma crystallization performance.

1. Introduction

In recent years, the application fields of functional coatings have been expanding widely. Functional coatings 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 a poor heat-resistance in general and crystalline films are, therefore, difficult to be deposited on them.

For preventing the plastic substrates from thermal damage, a pulse-laser-induced melt-regrowth method has been developed in order to crystallize amorphous silicon films deposited on plastic sheet substrates with a heat-barrier layer for TFT circuit construction in flexible displays [1]. However thermal processes are sometimes 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) and that of deposited inorganic materials. This difference in thermal expansion coefficients should be one of the causes of the problems encountered in the production of fine pattered devices [2].

Sol–gel technology can synthesize various inorganic materials and printing technology of sol–gel solutions shows a tremendous progress for realizing pattered coating at room temperature [3]. Still, for its real adaptation to the production, the most desired is sophisticated densification/crystallization technology because high-temperature heating is inevitable for sol–gel film finishing in conventional processes.

We have developed a crystallization technology using RF plasma; various amorphous films were crystallized and densified by less-than-5-minute treatment, without severe raise of film temperature. In this paper, we will summarize the results obtained on the plasma-crystallization and discuss the possible mechanism of the crystallization.

2. Experimental

Sol–gel derived 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″ 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.

Sputtered amorphous TiO_2 films were prepared by DC (direct current) sputtering of a Ti metal target (3 N purity) on soda-lime glass with 20 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.

Amorphous ITO films were deposited by DC sputtering method on soda-lime glass and PET substrates with a 15 or 20 nm-thick SiO_2 alkali-barrier layer. The ITO films were deposited using a ceramics

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doi:10.1016/j.tsf.2008.11.086

target having a 90 wt.% In_2O_3–10 wt.% SnO_2 composition and a sputter gas of 3% O_2 diluted with Ar.

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. The sputter target used is a Si polycrystalline with a ca. 1×10^{-3} ohm cm resistivity and Ar gas including 5% H_2 was used as a sputter gas.

The thickness of the films was measured using a stylus-type surface tracer (Veeco Instruments Inc., Dektak IIA). The crystalline structure of films was evaluated by asymmetric XRD (X-ray diffraction) method employed Seemann–Bohlin arrangement with a fixed angle of 0.8° between the incident X-ray beam and the TiO_2 or ITO film surface and 0.25° for silicon films: XRD machine used is RINT-2100 (Rigaku Co.) with CuK_{alpha} operated at 40 kV–30 mA.

The films were placed in a center of a barrel-type quartz or borosilicate chamber having a pair of electrodes each covering half of the cylinder wall. The films were electrically floated, that is, were neither connected electrically to the electrodes nor to electric ground. Then, RF power was supplied by a solid state 13.56 MHz RF power generator (Huettinger Elektronik GmbH + Co. KG, QINTO 3013) through an auto impedance matcher (RF VII, Inc.) and the films were treated with capacitively coupled RF plasma. In some cases, 0.15 mm thick Cu sheets were attached to the backside of the glass substrate, which was also electrically floated from the electric ground. The film temperature during the plasma treatment was measured by using a radiation thermometer (IT-540 N, Horiba Ltd.) and its reproducibility was about plus or minus 4°.

3. Results and discussion

3.1. Crystallization by O_2 plasma treatment

XRD profiles of titanium-alkoxide derived TiO_2 film coated on silicon wafers with and without 10-minute O_2 plasma treatment (plasma gas pressure being 330 Pa) and with heat treatment (at 500 °C for 1 h) are shown in Fig. 1. It can be found from Fig. 1 that the amorphous TiO_2 film was crystallized to anatase TiO_2, low-temperature crystalline-phase, by the RF plasma treatment. It is noted that the diffraction peaks around 20–22 of 2-theta of heat-treated TiO_2 film do not correspond to any of the peaks of TiO_2 crystalline polymorphs. While plasma-treatment around 330 Pa of plasma gas pressure transformed all the prepared TiO_2 films from the titanium-alkoxide to anatase TiO_2, amorphous TiO_2 films treated at a far different gas pressure from 330 Pa were not crystallized, as indicated in our previous article [4].

Fig. 2 represents the XRD profiles around (222) bixbite In_2O_3 peaks obtained from150 nm thick ITO films deposited on soda-lime glass substrate and processed with O_2 RF plasma in various plasma gas pressures for 10 min. The experimental results revealed that the plasma gas pressure on the plasma treatment is the key parameter of the effective crystallization.

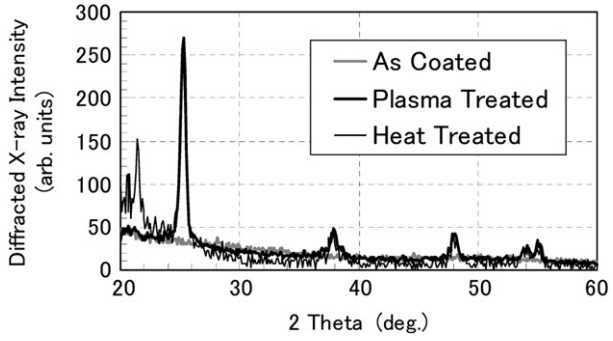

Fig. 1. X-ray diffraction profiles of sol–gel derived TiO_2 film before and after O_2 plasma treatment at 330 Pa for 10 min. The profile of the TiO_2 film heat-treated at 500 °C for 1 h is also represented.

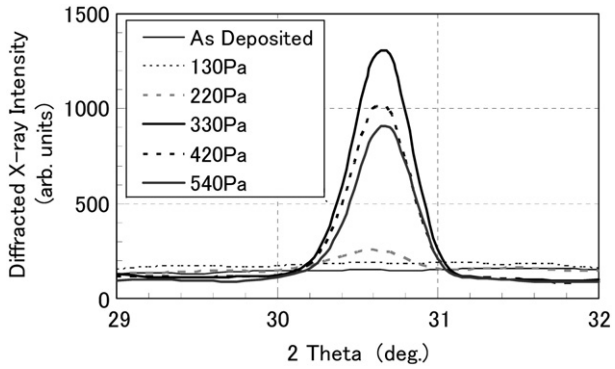

Fig. 2. X-ray diffraction profiles around (222) bixbite peak of sputtered ITO films treated with O_2 plasma in various plasma gas pressure for 10 min. The profile of as-deposited ITO film is also represented.

In the case of O_2 plasma treatment, both the titanium-alkoxide derived TiO_2 films coated on silicon wafers and ITO films sputter-deposited on soda-lime glass substrates were effectively crystallized around 330 Pa of plasma gas pressure. Therefore, it can be concluded that the most appropriate gas pressure (330 Pa) is independent to the film preparation method and film and substrate materials.

3.2. Crystallization by Ar plasma treatment

Fig. 3 represents the (222) bixbite In_2O_3 peaks of ITO films treated by Ar plasma with various plasma gas pressures for 10 min. It is found from Fig. 3 that the effective plasma pressure in the case of Ar plasma treatment is around 1000 Pa and is different from that of O_2 plasma treatment case (330 Pa). The most appropriate Ar plasma gas pressure was around 790 Pa, as was statistically found from more-than-500 plasma-crystallization experiments on ITO films deposited on soda-lime glass. XRD profiles of ITO film deposited on PET substrate with 20 nm thick SiO_2 barrier layer are represented in Fig. 4. It is noted that the large peaks at 2-theta of 26° in Fig. 4 derive from the PET substrate and do not change their shape and position by the plasma treatment.

The most effective plasma gas pressure is the same as that for Ar plasma crystallization of hydrogen-doped amorphous silicon (a-Si:H) films, as shown in Fig. 5 [5]. These experimental results on ITO and a-Si:H indicate that the appropriate gas pressure is independent to the film and substrate materials also in the case of Ar plasma treatment and the pressure is around 790 Pa.

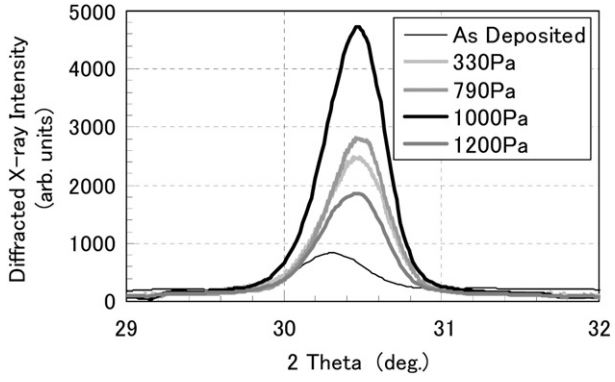

Fig. 3. X-ray diffraction profiles around (222) bixbite peak of sputtered ITO films treated with Ar plasma in various plasma gas pressure for 10 min. The profile of as-deposited ITO film is also represented.