Photoluminescence at room temperature in amorphous SrTiO₃ thin films obtained by chemical solution deposition

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Abstract

Intense photoluminescence in highly disordered strontium titanate amorphous thin films prepared by the polymeric precursor method was observed at room temperature (300 K). The luminescence spectra of SrTiO₃ amorphous thin films at room temperature revealed an intense single-emission band in the visible region. X-ray absorption near edge structure was used to probe the local atomic structure of SrTiO₃ amorphous and crystalline thin films. Photoluminescence intensity in the 535 nm range was found to be correlated with the presence of non-bridging oxygen defects. A discussion is presented of the nature of this photoluminescence, which may be related to the disordered structure in SrTiO₃ amorphous thin films.

Keywords: Thin films; Amorphous thin films; Photoluminescence; SrTiO₃

1. Introduction

There is much interest in the areas of science and technology in perovskite-type structured compounds with the chemical ABO₃ formula (A and B are cations while O is the oxygen anion), owing to their wide range of electronic applications [1–4]. Within this class of compounds, SrTiO₃ and BaTiO₃, in their crystalline form, display a semiconductive behavior. In addition, when pure SrTiO₃ and BaTiO₃ samples are excited by radiation above their energy band gaps, which normally range from 3.0 to 3.2 eV for BaTiO₃ and 3.4 eV for SrTiO₃, a broad luminescent band appears at low temperatures [5,6].

SrTiO₃ is a well-known perovskite-type paraelectric oxide with a large dielectric constant, which has recently attracted a good deal of attention due to its excellent dielectric, photoelectric and optical properties [7]. Although these compounds in amorphous phase form have been exhaustively studied [8,9], photoluminescence (PL) at room temperature has not yet been reported on. Ewer since Canham [10] first observed visible photoluminescence at room temperature in porous silicon, the study of photoluminescence in disordered or nanostructured materials has focused on the development of new electro luminescent materials, owing to its potential technological applications, which include flat-screen full-color displays. The amorphous PbTiO₃ powder studied by Leite et al. [11,12] and prepared by a sol–gel method also showed a broad photoluminescent band at room temperature. Leite et al. ascribed this photoluminescence to defects, resulting from the disordered structure of the amorphous PbTiO₃ powder, such as NBO (non-bridging oxygen).

This paper reports on measurements of broad, intense photoluminescence observed at room temperature in SrTiO₃ amorphous thin films prepared at low temperatures and obtained by the polymeric precursor method [13–15].

2. Experimental

SrTiO₃ amorphous thin films were processed by the polymeric precursor method. A flow chart of the SrTiO₃ synthesis used in this study is outlined in Fig. 1. Titanium citrates were formed by dissolution of titanium isopropoxide in an aqueous solution of citric acid (60–70 °C). After
homogenization of the Ti solution, SrCO$_3$ was slowly added and after complete dissolution of the SrCO$_3$ salt, ethylene glycol was added to promote polymerization of the mixed citrates by polyesterrification reaction. The molar ratio between the strontium and titanium cations was 1:1, the citric acid/metal ratio was fixed at 1.00, and the citric acid/ethylene glycol ratio was fixed at 60/40 (mass ratio).

Platinum-coated silicon was used as a substrate. This substrate was spin-coated by dropping a small amount of the polymeric precursor solution onto it. Rotation speed and spin time were fixed at 4000 rpm and 30 s, respectively. After deposition, each layer was dried at 150 °C on a hot plate for 20 min to remove residual solvents.

The heat treatment was carried out in tube furnace in an oxygen flow at a heating rate of 5 K min$^{-1}$ up to 200 °C for 8 h to pyrolyze the organic materials.

The SrTiO$_3$ films were structurally characterized by X-ray diffraction (XRD) (Cu K$_\alpha$ radiation). The diffraction patterns were recorded on a Siemens D5000 machine in a $\theta$-2$\theta$ configuration, using a graphite monochromator. The microstructural characterization was performed by atomic force microscopy (AFM) to obtain a three-dimensional image reconstruction of the sample’s surface, using a Digital Instruments Multi-Mode Nanoscope IIIa. The film thickness was measured by a thin film cross-section analysis made by scanning electron microscopy (Zeiss, DSM940A).

Ti K-edge XANES spectra were collected at the facilities of the NLSL (National Laboratory of Synchrotron Light) in Campinas, SP, Brazil. The NLSL storage ring was operated at 1.36 GeV and 60–100 mA. Data were collected at the Ti K-edge (4966 eV) in the total electron yield mode for thin film samples. The beam was monochromatized using a Si(1 1 1) channel cut monochromator with an energy step equal to 0.5 eV. Crystal $\beta$-Ba$_2$TiO$_3$, Ba$_2$TiSi$_2$O$_8$ (fresnoite) and r-TiO$_2$ (rutile) powder was used as a structure reference. The Ti atoms in this structure are coordinated by 4, 5 and 6 oxygen atoms, respectively.

The photoluminescence spectra of the SrTiO$_3$ amorphous thin films was taken with a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. The 488.0 nm exciting wavelengths of an argon ion laser were used with the maximum output power of the laser kept at 20 mW. A cylindrical lens was used to prevent the sample from overheating. The slit width used was 100 µm. All the measurements were taken at room temperature.

3. Results and discussion

Fig. 2 shows the XRD patterns of the SrTiO$_3$ amorphous thin films deposited on platinum-coated silicon substrate.
and annealed at a low temperature (200 °C) for 8 h in an oxygen flow. A diffuse XRD pattern can be observed, indicating the formation of an inorganic amorphous precursor after the pyrolysis process. The peaks observed are platinum substrate. In addition, the SrTiO3 powder obtained by the polymeric precursor method also showed the formation of an amorphous inorganic phase, which was revealed, respectively, by XRD and infrared spectroscopy analyses.

Fig. 2 shows three- and two-dimensional images of a SrTiO3 film annealed at 200 °C for 8 h in an oxygen flow and compares them with a SrTiO3 crystalline thin film. The amorphous thin film was characterized by a smooth surface...
Fig. 4. Ti K-edge XANES spectra of the SrTiO$_3$ thin films: (a) crystalline and (b) amorphous.

The surface roughness was 0.25 nm. SrTiO$_3$ amorphous thin films with a thickness of 70 nm were obtained.

The structure of SrTiO$_3$ amorphous and crystalline thin films were also characterized using X-ray absorption near-edge structure (XANES) spectroscopy. Fig. 4 shows the Ti K-edge XANES spectra of the SrTiO$_3$ thin film crystallized at 600$^\circ$C for 2 h compared to the SrTiO$_3$ amorphous thin film. In the amorphous film, a pre-edge feature of a Ti K-edge XANES spectra located at approximately 4970 eV can be observed. This peak is related to the 1s $\rightarrow$ 3d transition and is usually attributed to energy level transition from Ti 1s to the Ti 3d/O 2p molecular orbital. Farges [16] made an experimental study of the 1s $\rightarrow$ 3d transition as a function of Ti coordination. Based on the 1s $\rightarrow$ 3d energy position and normalized intensity, Farges obtained structural information of the Ti atoms in crystalline and glassy fresnoites. Using a similar approach, we were able to obtain information on Ti atom coordination in our samples. This study showed that SrTiO$_3$ amorphous thin films are formed basically through oxygen Ti coordination five (TiO$_5$ —square base pyramid), with a small number of Ti atoms in coordination six (TiO$_6$ —octahedron). In addition, in the SrTiO$_3$ amorphous thin films, $\sim$80% of the Ti atoms are coordinated by five oxygen (TiO$_5$). Similar XANES spectra of SrTiO$_3$ crystalline thin films were obtained by Ravel and Stern [17].

Fig. 5 shows the photoluminescence spectra of SrTiO$_3$ amorphous thin films, which present a broad, intense band, taken at room temperature. As can be seen in Fig. 5, the SrTiO$_3$ crystalline thin films showed no sign of photoluminescence. This behavior can be explained as follows. As the material begins to become ordered (in crystalline form), the intensity of photoluminescence drops to virtually zero at room temperature. Thus, if the photoluminescent signal is correlated with the disordered structure (SrTiO$_3$ amorphous thin film), it is generally believed that, when the system becomes ordered, the photoluminescent signal disappears, an assumption that is confirmed by the curve in Fig. 5b. In addition, TiO$_5$ - and TiO$_6$ -type structures were found in the amorphous system, since the photoluminescent signal relates to the presence of TiO$_6$ -type structures in an amorphous matrix, which was confirmed by XANES. Hence, the decrease of photoluminescence between 200 and 600$^\circ$C is correlated with the decrease or even the extinction of the TiO$_6$ -type structures, with the resulting reduction in the number of NBO-type defects (non-bridging oxygen) and in the photoluminescent signal. In addition, based on experimental results obtained by XANES analysis, Leite et al. [11] postulated that amorphous lead titanate is formed of a Ti-O network and the charge of the lead cation must be compensated by negatively charged NBO. These positively charged defects lead to possibly different valence states of the Ti ion (Ti$^{4+}$ and Ti$^{3+}$). This finding is a good indication that the photoluminescence of SrTiO$_3$ amorphous thin films obtained by the polymeric precursor method stems from the inorganic disordered phase. This, in turn, strongly suggests that the disordered phase in which NBO is present (as the principal defect) may be responsible for strong visible photoluminescence.

4. Conclusions

Summarizing, intense visible photoluminescence at room temperature was observed in highly disordered SrTiO$_3$ amorphous thin films obtained at a low temperature (200$^\circ$C) and prepared by the polymeric precursor method. The nature of the above-described results is not yet clear, but may be related to the disordered structure of amorphous thin films, such as coordination five between O-Ti and coordination six between O-Ti structures, as indicated by the results of our XANES analysis, or by defects promoted by NBO or impurities. In addition, processing of these thin films requires neither expensive equipment and reagents, nor any special
atmosphere control, nor even a high vacuum chamber for thin film deposition. To conclude, the results of our studies of the intense photoluminescence of SrTiO₃ amorphous thin film indicate that this material is a highly promising candidate for optoelectronic applications.

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References