≪Research Paper≫ Applied Science and Convergence Technology Vol.23 No.5, September 2014, pp.261-264
http://dx.doi.org/10.5757/ASCT.2014.23.5.261

Room-Temperature Luminescence from Ion Beam or Atmospheric Pressure Plasma-Treated $SrTiO_3$

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(Received September 19, 2014, Revised September 28, 2014, Accepted September 30, 2014)

$SrTiO_3$ (STO) single crystal irradiated with a 3-MeV proton beam exhibits blue and green mixed luminescence. However, the same proton beam when used to irradiate STO with a very thin layer of deposited Pt does not show any luminescence. This Pt layer prevents any damage which may otherwise be caused by arcing, which stems from the accumulated surface voltage of tens of kV due to the charge induced by secondary electrons on the surface of the insulator during the ion beam irradiation process. Hence, the luminescence of ion-irradiated STO originates from the modification of the STO surface layer caused by arcing rather than from any direct ion beam irradiation effect. STO treated with atmospheric-pressure plasma, a simple and cost-effective method, also exhibits the same type of blue and green mixed luminescence as STO treated with an ion beam, as the plasma also creates a layer of surface damage due to arcing.

Keywords : $SrTiO_3$, Atmospheric pressure plasma, Ion beam, Photoluminescence

I. Introduction

Strontium titanate, i.e., $SrTiO_3$ (STO), a cubic-perovskite-structured compound with a wide bandgap (e.g.,=3.2 eV), is an important material in modern technology applications such as photocatalysis [1], tunable microwave applications [2], oxygen sensors [3], insulating films for electronic devices [4], ReRAM (resistive random access memory) [5], and others. It can be also used as a substrate for other perovskite-structure thin films, such as high-temperature superconducting materials [6].

The photoluminescence (PL) of STO has many interesting effects. For example, stoichiometric STO shows different PL emissions as the temperature is changed. STO shows no PL emission at room temperature. However, it emits green and infrared PL when cooled to a low temperature at $T < 110$ K. In addition, blue luminescence in an oxygen-deficient layer which had undergone surface damage introduced by Ar^+ irradiation at an energy level of 300 eV at room temperature was reported by Kan et al. [7] Recently, Rho et al. reported that C^- and H^+ irradiation at energy of 3 MeV also emits green, blue, and infrared-PL at room temperature [8,9].

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II. Experimental Details

An undoped STO single crystal was used in the experiment. STO were coated with normal and thin Pt layers (less than 10 nm) at room temperature with 3-MeV proton ion irradiation at irradiation doses of 3.75×10^{12} and 7.5×10^{12} ions/cm^2, respectively. In order to prevent possible heating caused by the ion beam, the proton flux was kept below 1 nA/cm^2. The direction of the incident ion beam was tilted by 7° in the surface normal direction to prevent possible channeling during the ion implantation process. The atmospheric-pressure plasma treatment was processed on the same STO substrate at different times (10 min, 20 min, and 10 h). The photoluminescence spectrum was measured using a HORIBA spectrometer (Fluorolog-3) equipped with 325 nm He-Cd laser (power=25 mW/cm^2).

III. Results and Discussion

The photoluminescence (PL) spectra of the STO single crystal irradiated with 3-MeV proton ions at doses of 3.75×10^{12} and 7.5×10^{12} ions/cm^2 are plotted in Fig. 1. There is a main broad signal at 400~500 nm and a small peak at 800 nm. The main peak intensity increases as the proton dose increases. The inset shows the picture taken of a sample irradiated at a dose of 3.75×10^{12} ions/cm^2 during the PL measurement process. As shown in this inset, luminescent spots less than a few mm in size do not uniformly cover the entire surface area of such samples irradiated at a low dose. The creation of irregular separate spots is an extraordinary phenomenon, as ion-beam irradiation generally creates uniform damage. Nevertheless, as the ion dose increases, the number of luminescent points increases until finally the entire the surface area exhibits luminescence due to the superposition of the luminescent spots [9].

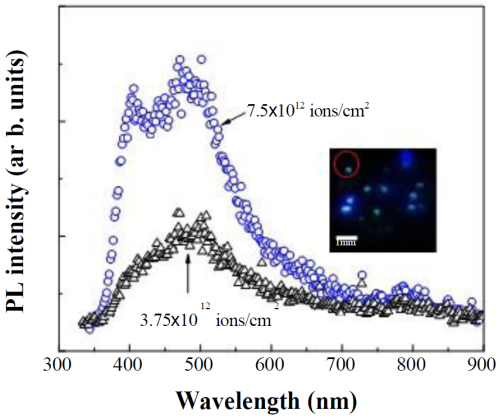

Figure 1. PL-spectrum of a STO single crystal irradiated with 3-MeV protons. The inset shows an image of the PL-irradiated STO taken with a digital camera.

Kan and Rho et al. reported nearly the same damage to a layer with a thickness of 15~23 nm below the surface, as investigated by transmission electron microscopy, even with extremely different levels of irradiation energy of 300 eV and 3 MeV; the luminescence came from the defect level of the damaged layer with oxygen vacancies induced by the ion beam. The mean projected range for the STO sample Ar^+-irradiated at 300 eV is 1.1 nm, and most of the ions reside at 2.5 nm according to SRIM (stopping and range of ions in matter) simulation [10] results. Therefore, the generation of an amorphous layer and an oxygen-deficient layer near the surface of the STO with a thickness of 23 nm cannot be a direct effect of the 300-eV Ar ion irradiation. Fig. 2 shows the SRIM simulation result of the mean projected range and the damage profile of the STO irradiated with 3-MeV proton ions. The mean projected range for the STO irradiated with 3-MeV proton ions is 50 μm, and most of the damage exists in the projected range of the ion beam. In addition, the high-energy (MeV) light ions do not cause damage due to their very small elastic scattering cross-section. Therefore, the damaged layer with a thickness of 15 nm is on the top surface of the STO sample irradiated with the 3-MeV ion beam according to transmission electron micro-

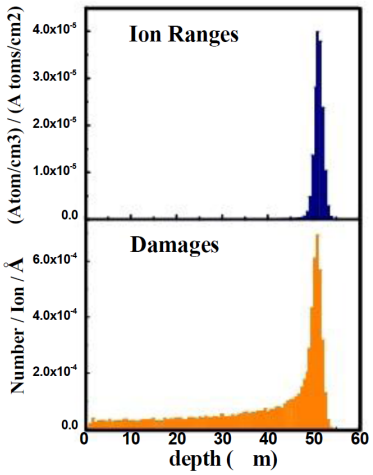

Figure 2. Projected range and damage profile of 3-MeV proton ion irradiation into STO according to the SRIM (stopping and range of ions in matter) simulation code.

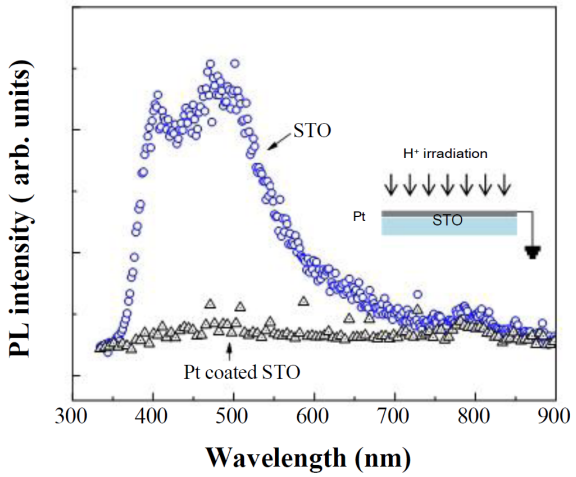

Figure 3. PL spectra of STO irradiated with a 3-MeV proton ion beam and Pt-coated STO.

scopy results [9]. This cannot be explained as a direct effect of the ion beam irradiation process.

It is well known that surface charging take place when an ion beam is irradiated into an insulator without an electron shower or charge drain with a thin metallic layer deposited onto the surface to prevent the ion beam charging effect. Kim et al. [11] reported that surface voltage levels of tens of kVs accumulate due to the charging of secondary electrons during the ion irradiation process into an insulator. If there is no current path from the surface to the ground, the accumulated charges will be discharged with electrical arcing, which will cause damage to the surface. This phenomenon can arise with our sample, as undoped STO is an insulator itself. In order to confirm the relationship between electrical arcing and damage and luminescence as well, a very thin Pt layer was deposited onto a STO substrate, i.e., an insulator itself, after which it was irradiated with 3 MeV proton projectiles. The PL spectrum and a schematic diagram of this experiment are shown in Fig. 3. The thickness of the Pt layer is less than 10 nm and therefore should not affect the ion beam energy transfer and lead to the generation of damage. In addition, the Pt layer is grounded completely to prevent the accumulation of an electrical charge during the irradiation process. As shown in the PL spectrum in Fig. 3, no luminescence is detected from the Pt-coated sample despite the fact that it was irradiated by a 3-MeV proton ion beam at the same dose. This implies that the Pt layer prevents electrical discharge arcing and thus prevents damage to the surface. Thus, the ion-beam-induced luminescence comes from the damaged layer, as caused by electrical arcing due to the accumulated potential charge of tens of kV and not directly from ion-beam-induced damage itself. The extraordinary irregularly separated luminescence spots shown in the inset of Fig. 1 are clearly understandable, as electrical arcing takes place in a random and non-uniform manner. Ion irradiation is a well-defined and clean process that is compatible with the fabrication of Si devices. However, it is a very expensive technique. An atmospheric-pressure plasma treatment is a very cost-effective process, as a reaction vessel is not needed to ensure the maintenance of the pressure level, which can differ due to the atmospheric pressure. The system generates an electric arc on the surface of a target in the form of a high-voltage discharge. Therefore, this method can damage the surface of an insulator. In order to clarify

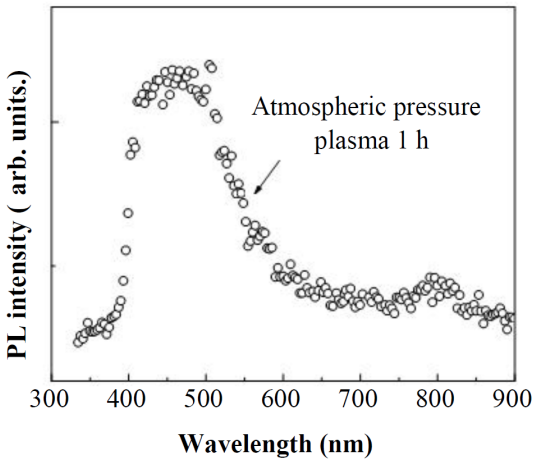

Figure 4. PL spectrum of a STO single crystal treated with atmospheric-pressure plasma.

our assumption, an atmospheric-pressure plasma treatment was carried out. Fig. 4 shows the PL data of STO samples treated with atmospheric-pressure plasma, inducing only discharge arcing. This sample also shows the same blue and green luminescence with a wavelength of 400～500 nm, like the ion-irradiated sample. It shows the same trends, in which the number of luminescent spots increases as the treatment time increases. This result also clearly supports the fact that discharge arcing causes structural changes in the STO surface region, which emits the luminescence.

IV. Conclusion

In summary, both ion-beam and plasma-treated STO samples exhibit blue and green luminescence with a wavelength of 400～500 nm. This luminescence stems from the damaged region induced by arcing on the surface caused by the accumulated potential discharge. An atmospheric plasma treatment is a viable alternative method with which to modify STO so that it emits luminescence in a cost-effective manner.

Acknowledgements

This work was supported by the Korea Institute of Science and Technology of Seoul (Grant No. 2V01742) and by a grant from the Nuclear Research and Development Program of the Korea Science and Engineering Foundation (KOSEF) funded by the Korean government (MEST, Grant Code: 20090067238). Additional support came from a grant from the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (2009007043).

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