Photocarrier Injection to Perovskite Manganites

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Abstract

We have fabricated (La, Sr)MnO_3 thin films on *n*-type $SrTiO_3$ substrates doped with Nb by means of the pulsed laser deposition technique. It is shown that hole carriers photogenerated in the substrates under UV light irradiation are injected efficiently to the films. By measuring the out-of-plane voltage of the heterojunction the surface density of hole carriers injected to (La, Sr)MnO_3 is estimated: It is at most 1.6×10^{13} cm^{-2}, but is improved up to 3.1×10^{13} cm^{-2} by modifying the junction structure, i.e., inserting a pure $SrTiO_3$ layer between the film and the substrate.

Keywords: Type your keywords here, separated by semicolons ; photocarrier injection;heterostructure;perovskite manganites; $La_{1-x}Sr_xMnO_3$

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It is well known that many interesting phenomena found in transition metal oxides (TMOs) are the consequences of hole doping into Mott insulators. Generally, the hole doping has been done by chemical substitutions of constituent elements as in $La_{1-x}Sr_xMnO_3$ ($0 < x < 0.6$) [1]. However, the chemical substitutions involve the randomness or distortions of the crystal structure. Very recently, Muraoka *et al*. reported an alternative method for external control of hole density in TMOs using ultraviolet (UV) light, which is photocarrier injection (PCI) in an oxide heterostructure [2.3]. Here we apply the PCI technique to manganese perovskites $La_{1-x}Sr_xMnO_3$ ($x = 0$, 0.1).

We have fabricated thin films of $La_{1-x}Sr_xMnO_3$ on the (001) surface of $SrTiO_3$ single crystal substrates doped with Nb. Two substrates with Nb concentration of 0.01 and 0.05 wt % were used. Epitaxial growth of $La_{1-x}Sr_xMnO_3$ was achieved by the pulsed laser deposition technique with a KrF excimer laser ($\lambda = 278$ nm). The film thickness was 100 nm. As the source of UV lights, a Xe lamp ($\lambda = 300$ - 400 nm) was used because its energy nearly corresponds to the optical band gap of $SrTiO_3$ (3.2 eV). The light irradiance was changed by using variable ND filters. The open-circuit photovoltage was measured at room temperature with electrodes of Au and In deposited on the film and substrate, respectively, in order to avoid the Schottky barrier formation at the interface.

We have carried out out-of-plane voltage measurements between insulating $LaMnO_3$ and $SrTiO_3$:Nb under light irradiation in order to verify hole doping into the film and estimate injected hole density. Figure 1 shows the UV irradiation dependence of open-circuit photovoltage (V_{OC}) for two samples with different Nb contents. A positive photovoltage to the $LaMnO_3$ film is observed in both the cases, which is the result of hole carrier injection to the film. The V_{OC} increases linearly with increasing light irradiance L in a wide rage of $10^{-4} < L < 1$ mW/cm^2 and tends to saturate at 0.2 V around 100 mW/cm^2. The surface density of holes is calculated approximately from the V_{OC} by integrating the equation $dQ = CdV_{OC}$, where Q is the accumulated electric charge per cm^2 (surface density) and C represents the electric capacitance of the junction. The C is obtained by assuming the formation of a depletion layer as in an ordinary *p-n* junction. Only the

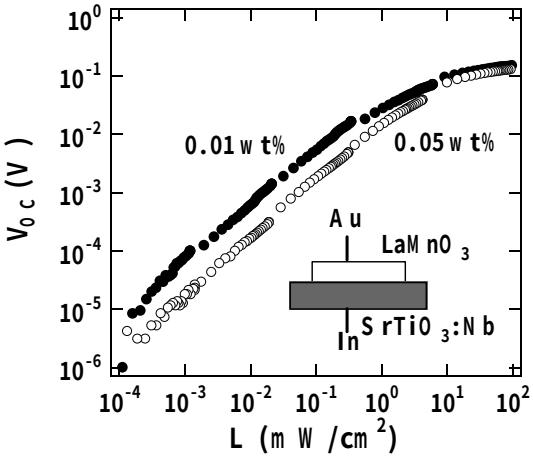

Fig. 1. Light irradiance dependence of out-of-plane open-circuit voltage for $LaMnO_3/SrTiO_3$:Nb(001), measured at room temperature. Two substrates with Nb content of 0.01 wt% (solid circles) and 0.05 wt% (open circles) was used.

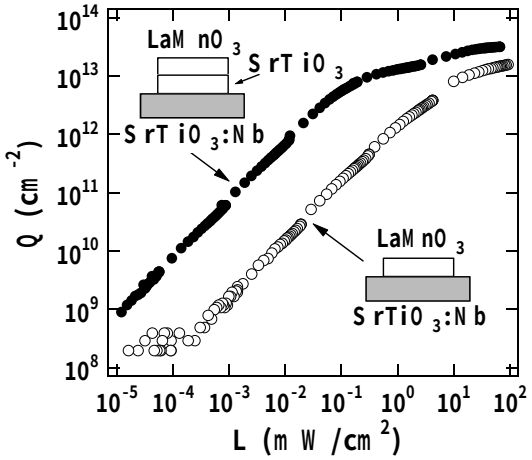

Fig. 2. Light irradiance dependence of surface density of holes injected to the film for $LaMnO_3/SrTiO_3/SrTiO_3$:Nb(0.05 wt%) (solid circles) and $LaMnO_3/SrTiO_3$:Nb(0.05 wt%) (open circles).

depletion layer in the substrate is taken into account, because the dielectric constant is much larger in the substrate than in the film. At the irradiance of 100 mW/cm^2, the surface density for Nb 0.01 wt% and Nb 0.05 wt% are 7.5×10^{12} cm^{-2} and 1.6×10^{13} cm^{-2},respectively. Assuming uniform distribution of holes ina 100-nm thick $LaMnO_3$ film, the maximum hole concentration per unit cell become 0.01 percent. At lower light illumination (0.1mW/cm^2) the surface density is almost the same, 2×10^{11} cm^{-2}, for the two cases. This means that the difference of Nb content in the substrate is not an important factor for the efficiency of injection. We carried out the same measurements for $La_{0.9}Sr_{0.1}MnO_3/SrTiO_3$:Nb and obtained almost the same results.

We have attempted to increase the hole density by modifying the band structure at the junction by inserting a pure $SrTiO_3$ layer (20 nm thick) between the film and substrate. Such a *p-i-n* junction structure is often utilized to solarcells for the purpose of improving the quantum efficiency. The saturated value of V_{OC} at high irradiance is increased to 1.2 V, in good agreement with the value expected from the band diagram for the *p-i-n* junction. Figure 2 indicates the UV light intensity dependence of surface density of holes for $LaMnO_3/SrTiO_3/SrTiO_3$:Nb(0.01 wt%). At low light irradiance it is about forty times as large as that of $LaMnO_3/SrTiO_3$:Nb. The maximum surface density is estimated to be 3.0×10^{13} cm^{-2} at 50 mW/cm^2 which is about twice larger than that (1.3×10^{13} cm^{-2} at 50 mW/cm^2) of the *p-n* junction. This enhancement may be due to the increment of both quantum efficiency and relaxation time of hole carriers.

In conclusion, we found hole carrier injection into $La_{1-x}Sr_xMnO_3$ (x = 0, 0.1) films using the photocarrier injection technique. The achieved maximum hole concentration is rather small, compared with those for other systems like VO_2/TiO_2:Nb [4] or $YBa_2Cu_3O_{7-\delta}/SrTiO_3$:Nb [4]. It is improved slightly by fabricating a *p-i-n* junction. However, further optimization of the band structure would achieve larger hole concentration. Moreover, it is expected that the hole concentration is increased dramatically at low temperature, because the lifetime of photocarrier can be long enough with cooling.

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