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Electrical properties of Sb-doped epitaxial SnO_2 thin films prepared using excimer-laser-assisted metal–organic deposition

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Abstract Excimer-laser-assisted metal–organic deposition (ELAMOD) was used to prepare Sb-doped epitaxial (001) SnO_2 thin films on (001) TiO_2 substrates at room temperature. The effects of laser fluence, the number of shots with the laser, and Sb content on the electrical properties such as resistivity, carrier concentration, and carrier mobility of the films were investigated. The resistivity of the Sb-doped epitaxial (001) SnO_2 thin film prepared using an ArF laser was lower than that of the film prepared using a KrF laser. The van der Pauw method was used to measure the resistivity, carrier concentration, and carrier mobility of the Sb-doped epitaxial (001) SnO_2 thin films in order to determine the effect of Sb content on the electrical resistivity of the films. The lowest resistivity obtained for the Sb-doped epitaxial (001) SnO_2 thin films prepared using ELAMOD with the ArF laser and 2 % Sb content was 2.5×10^{-3} Ω cm. The difference between the optimal Sb concentrations and resistivities of the films produced using either ELAMOD or conventional thermal MOD was discussed.

1 Introduction

Transparent conductive thin films are very important materials used to manufacture electronic, optical, and solar cell applications. Polycrystalline indium tin oxide (ITO) is commonly used to manufacture such applications because it is produced using low-temperature physical vapor processes; hence, it exhibits low resistivity. Inexpensive, highly conductive, transparent thin films are expected to be used in order to develop several next-generation applications. Using epitaxial thin films is the key to improving the electrical and optical properties of such applications because these properties strongly depend on the growth orientation of the thin-film materials. Therefore, it is very important to control the growth orientation of transparent, conductive, functional-oxide thin-film materials. Most methods of growing epitaxial functional-oxide thin films require the use of both a vacuum and high temperature, making device production expensive.

From the perspective of decreasing production cost, tin oxide is a promising alternative material to ITO for manufacturing next-generation electronic devices because it exhibits good properties such as high conductivity, transparency, and chemical stability [1, 2]. Moreover, it is an abundant natural resource. Therefore, we used excimer-laser-assisted metal–organic deposition (ELAMOD) to develop a method for producing metal-oxide thin films at low temperature and used it to produce SnO_2 thin films on various substrates [3-6]. In a previous study [5, 6], epitaxial SnO_2 thin films were prepared using an excimer laser to anneal amorphous SnO_2 films on (001) TiO_2 substrates. Both the amorphous tin oxide and the TiO_2 substrate absorbed the laser energy, and the SnO_2 thin films epitaxially grew on the TiO_2 substrate by photochemical and photothermal reactions. Further, direct irradiation of metal–organic compounds is a more effective method of epitaxially growing tin oxide thin films and enhancing the electrical properties of the films than using a laser to irradiate amorphous tin oxide, because the absorbance of metal–organic compounds is higher than that of amorphous tin oxide, which is prepared at 300 °C [7]. Therefore, the absorbance of precursor films used in ELAMOD is

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important for controlling the epitaxial growth of metal-oxide thin films and for enhancing the electrical properties of the thin films. To determine what effects ArF laser irradiation had on the crystallinity and electrical properties of epitaxially grown SnO_2 thin films, we investigated the photoreaction of metal–organic precursor films by irradiating them with an ArF laser in order to prepare epitaxial SnO_2 thin films at room temperature, and we characterized the crystallinity and electrical properties of the produced films. We also used ELAMOD to prepare epitaxial Sb-doped SnO_2 thin films that exhibited very low resistivity in order to investigate the effect of Sb content on the electrical properties of the thin films.

2 Experimental

A homogeneous precursor solution was prepared by mixing tin(II) 2-ethylhexanoate and SYM-Sb solution (a metal-oxide (MO) precursor material, Symetrix) at the appropriate concentration (Sb/(Sn + Sb) = 2–10 %) and viscosity for spin coating. The solution was spin coated onto single-crystal (001) TiO_2 substrates at 4,000 rpm. The MO precursor films were then dried at 100 °C in air to evaporate the solvent and were irradiated using an ArF laser (spot size 8 × 8 mm; pulse duration 20 ns) at 25 °C and 10 Hz for 200–500 shots. The films were spin coated and irradiated five times to increase the thickness of the films.

The obtained films were 200 nm thick. The crystallinity or epitaxy of the films was examined using X-ray diffraction (XRD, Cu-Kα1; MAC Science, MXP3A) θ–2θ scans. Cross-sectional transmission electron microscopy (XTEM) was performed using a high-resolution electron microscope (Hitachi H-9000, operated at 300 kV). Conventional methods (i.e., mechanical cutting, face-to-face gluing, mechanical grinding, polishing, dimpling, and Ar-ion milling at 4 kV) were used to prepare specimens for XTEM observation. The resistivity, carrier concentration, and carrier mobility of the Sb-doped SnO_2 thin films were measured using the van der Pauw method [8].

3 Results and discussion

We first used ELAMOD with an ArF laser to investigate the effect of laser fluence on the crystal growth of 10 % Sb-doped epitaxial SnO_2 thin films. Figure 1 shows the XRD patterns for the Sb-doped epitaxial SnO_2 thin films prepared using an ArF laser to irradiate the precursor films at various fluences for 300 pulses. Although crystalline thin films did not form on the (001) TiO_2 substrates irradiated at either 20 or 80 mJ/cm^2, the XRD spectrum for the specimen irradiated at 100 mJ/cm^2 exhibited peaks associated with the

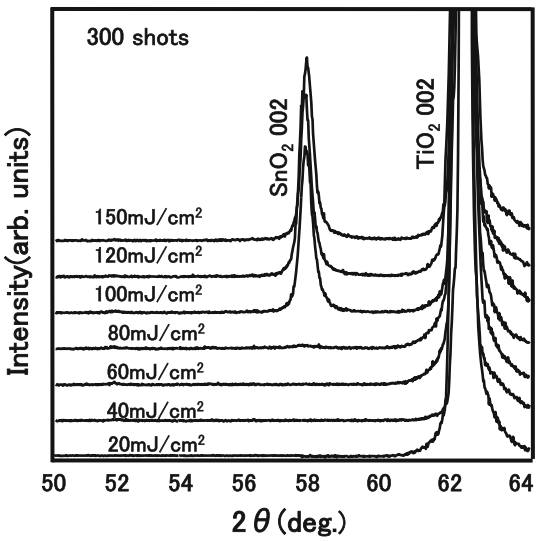

Fig. 1 XRD patterns for Sb-doped SnO_2 thin films prepared using ArF laser irradiation for various laser fluences

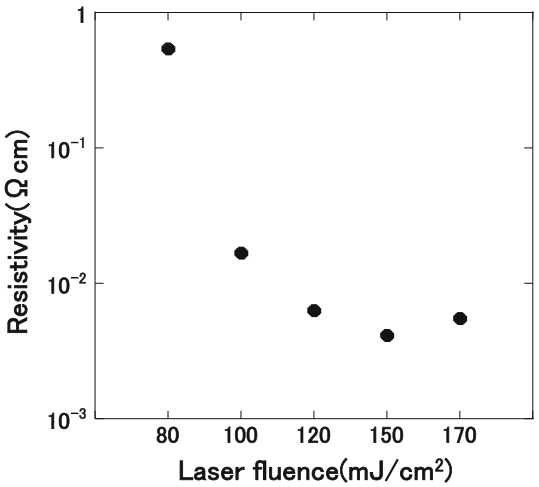

Fig. 2 Resistivity of Sb-doped SnO_2 thin films prepared using ELAMOD *plotted* as functions of laser fluence

(002) plane of SnO_2(JCPDS:041-1445) on the shoulder of the peak associated with the (002) plane of TiO_2. The intensity of the peaks associated with SnO_2 increased with increasing laser fluence to 120 mJ/cm^2. In a previous paper [7], we reported the growth of Sb-doped epitaxial (001) SnO_2 thin films prepared using KrF laser irradiation. When the KrF laser was used, an Sb-doped epitaxial (001) SnO_2 thin film did not form on the (001) TiO_2 substrate irradiated at 100 mJ/cm^2. However, an Sb-doped epitaxial SnO_2 thin film did form on the TiO_2 substrate irradiated at more than 150 mJ/cm^2 at room temperature. Thus, the ArF laser was more effective than the KrF laser for epitaxially growing SnO_2 thin films at lower laser fluences because the absorbance of metal–organic compounds is higher at 193 than at

248 nm. Figure 2 shows the resistivity of the 10 % Sb-doped epitaxial SnO_2 thin films prepared using ELAMOD plotted as functions of laser fluence. The resistivity of the Sb-doped SnO_2 thin film irradiated at 150 mJ/cm^2 was as low as 4.16×10^{-3} Ω cm.

To determine the effect of the number of shots from the laser on the resistivity of the 10 % Sb-doped epitaxial SnO_2 thin films, we irradiated the films with various numbers of shots from the laser. Figure 3 shows the XRD patterns for the Sb-doped epitaxial SnO_2 thin films prepared using the ArF laser to irradiate the precursor films for various numbers of shots. The peak associated with the (002) plane of epitaxial SnO_2 is exhibited on the shoulder of the peak associated with the (002) plane of TiO_2 in the XRD spectra for the thin films irradiated in the range 50–500 shots. The intensity of the XRD peaks for the films increased with increasing number of laser shots in the range 150–200 pulses. The intensity of the XRD peaks associated with the (002) plane of SnO_2 decreased for the thin films irradiated with 300 or more pulses. Further, the XRD peaks shifted to lower angles in the spectra for the films irradiated in the range 150–200 pulses and shifted to higher angles in the spectra for the films irradiated for 300 or more pulses.

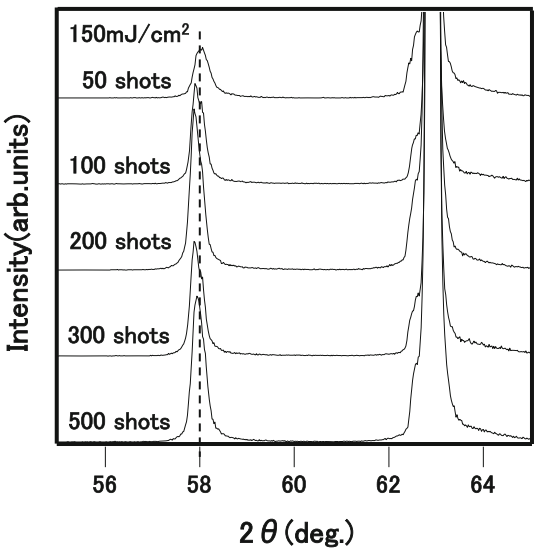

Fig. 3 XRD patterns for Sb-doped SnO_2 thin films prepared using ELAMOD for various numbers of shots with ArF laser

Figure 4 shows the resistivity (a), carrier concentration (b), and carrier mobility (c) of the 10 % Sb-doped epitaxial SnO_2 thin films prepared using ELAMOD plotted as functions of the number of laser shots. The minimum resistivity, carrier concentration, and carrier mobility of the films prepared using ELAMOD were 4.10×10^{-3} Ω cm, 4.26×10^{20}/cm^3, and 3.58 cm^2/V s, respectively, for the film subjected to 200 laser pulses. The resistivity of the films increased with increasing number of laser pulses to more than 500 pulses. On the basis of the carrier concentration and carrier mobility of the films, the increased resistivity of the films irradiated for 500 pulses is believed to be due to the change in the carrier mobility of the films. The carrier mobility of doped semiconductors is usually controlled by two major scattering mechanisms: grain boundary and ionized impurity scattering [9, 10]. On the basis of the XRD results, we believe that the change in the carrier mobility of the films was due to the formation of grain boundaries during laser irradiation. If the decreased carrier mobility of the films irradiated for 500 or more pulses was due to ionized impurity scattering from excess Sb ions doped into the SnO_2 thin films, the XRD peaks for the films irradiated for 500 or more pulses would have shifted to lower angles. The effect of Sb content on the carrier mobility of the Sb-doped epitaxial SnO_2 thin films is discussed in detail later. Irradiating Sb-doped epitaxial SnO_2 thin films at a high number of laser pulses does not improve the resistivity of the films.

We prepared 10 % Sb-doped SnO_2 thin films on TiO_2 substrates at 700 and 900 °C for 1 and 5 h, as shown in Fig. 5, to compare the films produced using either conventional thermal MOD or ELAMOD. The XRD spectrum for the film heated at 700 °C for 5 h exhibits a peak associated with the (002) plane of SnO_2 and other peaks associated with SnO_2. The XRD spectrum for the film

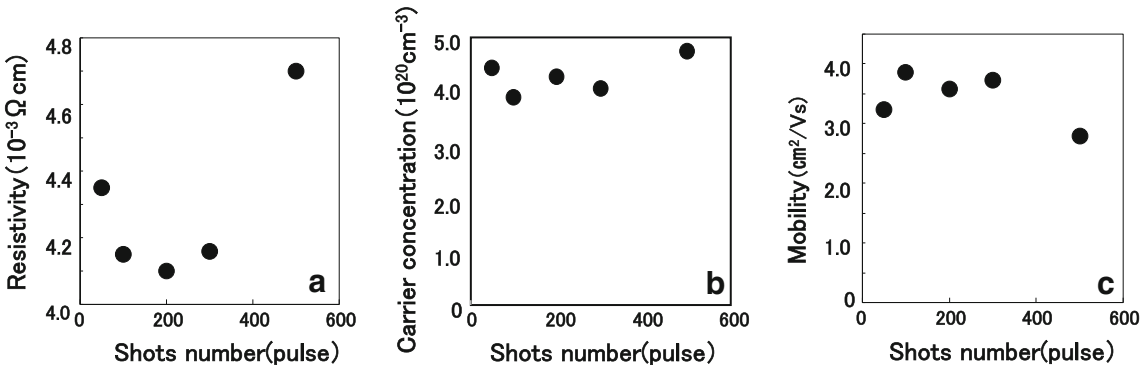

Fig. 4 Resistivity of Sb-doped SnO_2 thin films prepared using ELAMOD *plotted* as functions of number of shots with ArF laser

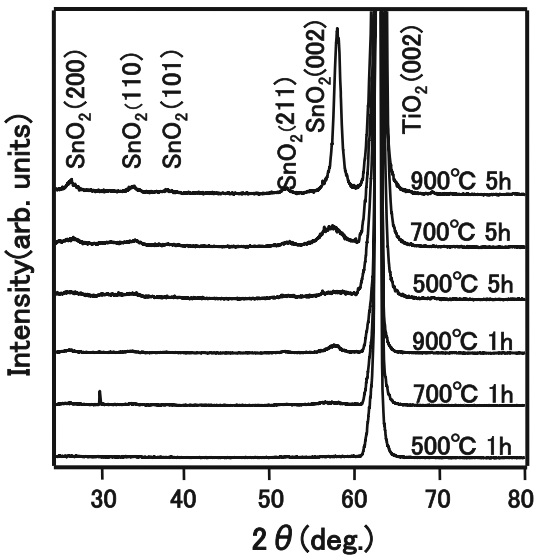

Fig. 5 XRD patterns for Sb-doped SnO_2 thin films prepared using thermal MOD

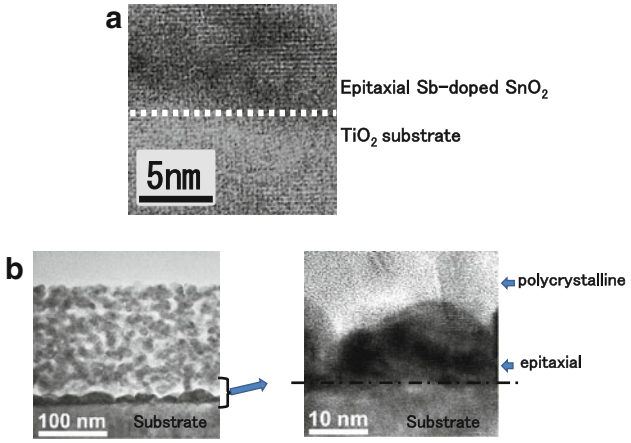

Fig. 6 XTEM images of films prepared using either **a** ELAMOD or **b** conventional thermal MOD

heated at 900 °C for 5 h also exhibits a peak associated with the (002) plane of SnO_2, and the peak is more intense than its counterpart in the XRD spectrum for the film heated at 700 °C for 5 h. However, the resistivities of the SnO_2 thin films prepared at 700 and 900 °C for 5 h were 7.24×10^{-3} and 1.31×10^{-2} Ω cm, respectively. Further, the carrier concentration and the carrier mobility of the 10 % Sb-doped SnO_2 thin film prepared at 700 °C for 5 h were $5.96 \times 10^{20}/cm^3$ and 1.45 cm^2/V s, respectively. The carrier mobility of the 10 % Sb-doped epitaxial SnO_2 thin film prepared using conventional thermal MOD was lower than that of the 10 % Sb-doped epitaxial SnO_2 thin film prepared using ELAMOD. On the basis of the XRD spectra for the films prepared using either conventional thermal MOD or ELAMOD, the crystals in the film prepared using conventional thermal MOD were not well oriented. Figure 6 shows XTEM images of the Sb-doped SnO_2 thin films produced using conventional either thermal MOD or ELAMOD. The entire film produced using ELAMOD epitaxially grew on the (001) TiO_2 substrate, as shown in Fig. 6a [7]. The film produced using conventional thermal MOD, on the other hand, epitaxially grew near the substrate surface and grew in a polycrystalline manner at the top of the film, as shown in Fig. 6b. The information obtained by comparing the epitaxial growth of the Sb-doped SnO_2 thin films produced using either conventional thermal MOD or ELAMOD with an excimer laser is very useful because it provides insight into different mechanisms of crystal growth. When a metal–organic precursor film was irradiated with the ArF excimer laser, the laser energy was absorbed into the film and substrate materials because the bandgaps of SnO_2 and TiO_2 are about 3 eV. In addition, the amount of mismatch between the (001) SnO_2 and (001) TiO_2 lattices was 0.8 %. Under these conditions, an epitaxial SnO_2 thin film grew from the interface between the precursor film and the TiO_2 substrate along the surface of the substrate. The epitaxial growth of the Sb-doped SnO_2 thin film produced using excimer laser irradiation in this study is the same phenomenon as that described in previous reports on the epitaxial growth of $La_{1-x}Sr_xMnO_3$ (LSMO) and lead zirconate titanate (PZT) thin films [11, 12]. When the Sb-doped SnO_2 thin film grown on the TiO_2 substrate was heated at a high temperature (700 °C), on the other hand, sufficient thermal energy was supplied to crystallize the entire film. Under this condition, the Sb-doped SnO_2 thin film simultaneously crystallized into a polycrystalline structure at the top of the film and an epitaxial structure near the surface of the TiO_2 substrate because the temperatures required for polycrystalline and epitaxial growth of SnO_2 are almost identical. Either controlling the film thickness or annealing the film for a long time at a temperature lower than that required for polycrystalline growth might be effective for epitaxial growth when using conventional thermal MOD to prepare epitaxial SnO_2 thin films. Thus, ELAMOD is an effective method of preparing epitaxial SnO_2 films at low temperature and in a short time.

To determine the effect of the Sb content on the resistivity of the Sb-doped epitaxial SnO_2 thin films, we prepared epitaxial Sb-doped SnO_2 thin films with various Sb contents. Figure 7 shows the XRD patterns for the Sb-doped epitaxial SnO_2 thin films prepared using laser irradiation for various Sb contents. The peak associated with the (002) plane of SnO_2 was continually shifted, when the Sb content changed to 4 % and then slightly decreased. Figure 8 shows the resistivity, carrier concentration, and carrier mobility of the Sb-doped epitaxial SnO_2 thin films prepared using ELAMOD plotted as functions of Sb content. The resistivity of the films increases with increasing

Sb content. The minimum resistivity of the Sb-doped epitaxial SnO_2 films prepared using the ArF laser was 2.8×10^{-3} Ω cm. The carrier concentration of the films increases with increasing Sb content. The carrier mobility of the films, on the other hand, decreases with increasing Sb content.

Another important result is that using ELAMOD with the ArF laser and 2 % Sb content to grow an Sb-doped SnO_2 epitaxial thin film yielded a film that was considerably more epitaxial than the films grown using ELAMOD and other Sb contents, and the resistivity of that film was as low as 2.5×10^{-3} Ω cm. For the films grown using conventional thermal MOD, 5 % Sb content is effective for decreasing the resistivity of the SnO_2 film [13–15].

To determine the optimal Sb content for the Sb-doped SnO_2 epitaxial thin films produced with either conventional thermal MOD or ELAMOD, we must consider the carrier concentration and the carrier mobility of the films. As previously mentioned, Hall carrier mobility in doped semiconductors is usually controlled by two major scattering mechanisms: grain boundary and ionized impurity scattering [9, 10]. On the basis of atomic force microscopy (AFM) measurements (not shown in this paper) of the surfaces of the films produced using ELAMOD under the same laser irradiation conditions (i.e., laser fluence, number of shots, and repetition rate), the surfaces of the films obtained for various Sb contents were almost identical. Therefore, the decrease in the Hall carrier mobility with increasing Sb content was not due to grain boundary scattering but was due to ionized impurity scattering. From the perspective of carrier mobility, low Sb content is effective for decreasing the resistivity of the films.

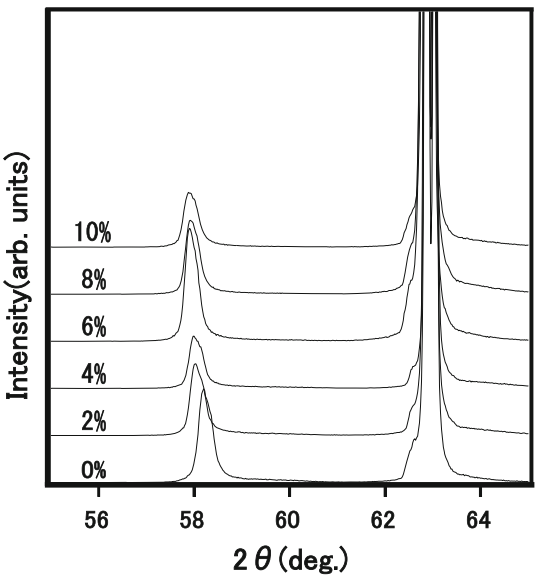

Fig. 7 XRD patterns for Sb-doped SnO_2 thin films prepared using laser irradiation for various Sb contents

However, the carrier concentration can generally be controlled with Sb doping. When SnO_2 thin films are doped with Sb, some of the Sn^{4+} ions in the lattice are replaced by Sb^{5+} ions, generating conduction electrons that decrease the resistivity of the film. So, high Sb content is effective for decreasing the resistivity of the Sb-doped SnO_2 thin films. Therefore, both the carrier concentration and the carrier mobility should be controlled to prepare the least resistive Sb-doped SnO_2 thin films.

Another important factor for controlling the carrier concentration in Sb-doped SnO_2 thin films is the formation of oxygen vacancies in the films. If oxygen vacancies form in SnO_2, they can also act as donor levels furnishing electrons into the conduction band. Therefore, the difference between the number of oxygen vacancies formed in the films produced with either ELAMOD or conventional thermal MOD would be due to the number of oxygen vacancies formed in the Sb-doped epitaxial films during laser irradiation. Organic materials were used as the starting materials in ELAMOD. When the organic materials were irradiated with the laser, the metal–organic material

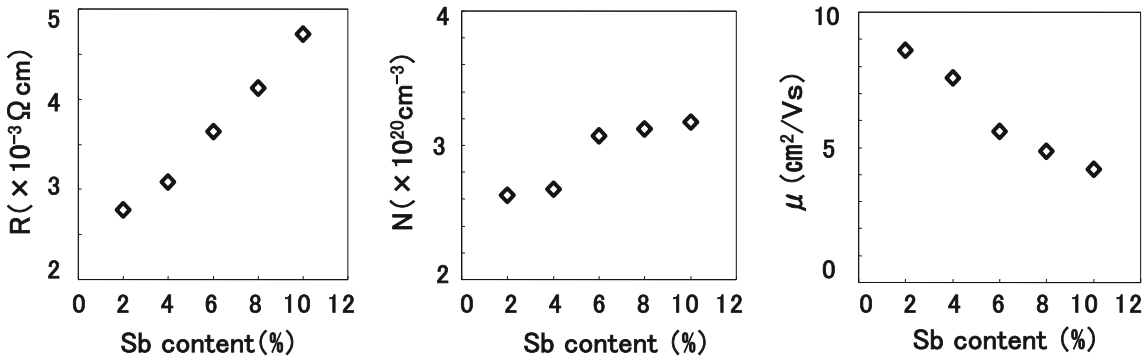

Fig. 8 Resistivity, carrier concentration, and carrier mobility of Sb-doped SnO_2 thin films prepared using ELAMOD *plotted* as functions of Sb content

decomposed and formed carbon during film formation. The carbon would decrease the oxygen concentration in the SnO_2 thin films when they were irradiated in air. The equation for the reaction between SnO_2 and carbon that produces oxygen vacancies in the films and carbon monoxide as a by-product is as follows:

$$SnO_2 + C \rightarrow SnO_{2-y} + CO_2 \quad (1)$$

The change in the resistivity of oxide materials such as VO_2 because of laser irradiation has previously been reported [16]. That would be why the SnO_2 thin film produced using ELAMOD and 2 % Sb content exhibited the lowest resistivity. Thus, ELAMOD is an effective method of decreasing the oxygen content in metal-oxide thin films and of forming less-resistive Sb-doped epitaxial SnO_2 thin films, without the need for a vacuum system.

4 Conclusions

Excimer-laser-assisted metal–organic deposition (ELAMOD) with an ArF laser was used to prepare Sb-doped epitaxial (001) SnO_2 thin films on (001) TiO_2 substrates at room temperature. The resistivity of the Sb-doped epitaxial (001) SnO_2 thin film prepared using the ArF laser was lower than that of the film prepared using a KrF laser. The van der Pauw method was used to measure the resistivity, carrier concentration, and carrier mobility of the Sb-doped epitaxial (001) SnO_2 thin films in order to determine the effect of Sb content on the electrical resistivity of the films. The lowest resistivity obtained for the Sb-doped epitaxial (001) SnO_2 thin films prepared using ELAMOD with an ArF laser and 2 % Sb content was 2.5×10^{-3} Ω cm. ELAMOD is useful for epitaxially growing Sb-doped (001) SnO_2 thin films at low temperature.

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