Microstructural evolution and electrical property of Ta-doped SnO$_2$ films grown on Al$_2$O$_3$(0001) by metalorganic chemical vapor deposition

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Abstract

Ta-doped tin oxide, SnO$_2$, films have been deposited using metalorganic chemical vapor deposition system on sapphire (0001) substrates in temperature range of 400 – 600$^\circ$C. When Ta concentration is varied from 0 to 8.30 at.% in the films, the electrical resistivity is changed by three orders of magnitude where the minimum resistivity was observed at 1.35% of Ta. An increase in the carrier concentration is a dominant factor responsible for such a large decrease in the resistivity while improved crystalinity contributes to the improvement in the mobility among doped samples. Microstructural investigation revealed the Ta-doped film showed a clean epitaxial relationship of SnO$_2$(100)/\textbackslash Al$_2$O$_3$(0001) with SnO$_2$(100)/\textbackslash Al$_2$O$_3$(1210) between the substrate and the film while undoped film had a weak epitaxial correlation with an extra epitaxial relationship of SnO$_2$(100)/\textbackslash Al$_2$O$_3$(0001) with SnO$_2$(010)/\textbackslash Al$_2$O$_3$(1100).

Keywords: Ta-doping; SnO$_2$; MOCVD; Epitaxy

1. Introduction

SnO$_2$ is an oxide semiconductor with unique electrical and optical properties [1,2] with a wide usage in commercial applications including display devices and gas sensors. Each application requires unique microstructure of the films. For instance, the gas sensing mechanism is mainly governed by the contact potential built at grain boundaries induced by the chemisorbed oxygen species. Thus, thin films with high porosity would provide good sensitivity with fast response [3]. As a transparent conductor, it is necessary to create electron degeneracy by introducing non-stoichiometry or appropriate dopants such as Sb or F to reduce the resistivity without sacrificing the optical transparency [4].

Many thin films fabrication techniques have been applied to prepare SnO$_2$-based thin films with various dopants [4,5]. However, reports on epitaxial SnO$_2$ thin films are limited [6,7]. By adopting advanced fabrication techniques in the semiconductor field as well as the substrate geometry, films with different types of microstructure can be manufactured based on application requirements. Our earlier publication includes variant structure in undoped SnO$_2$ thin films grown on Al$_2$O$_3$(0001) substrates [7]. This article reports the microstructural evolution in SnO$_2$ thin films when the films were doped with Ta, where Ta acted as an n-type dopant in SnO$_2$ to decrease the resistivity by increasing the carrier concentration.

2. Experimental procedures

The deposition of the films was carried out using a cold-wall, horizontal, low-pressure metalorganic chemical vapor deposition (MOCVD) system equipped with a pyrolytic graphite heater encased in pyrolytic boron nitride. Commercially available tin-tetra-butoxide, Sn(OC$_4$H$_9$)$_4$ and tantalum-ethoxide, Ta(OC$_3$H$_7$)$_5$, were used as the metalorganic sources. Each individual metalorganic gas was mixed at a mixing line and introduced into a quartz reactor through an inlet flange. Ultra high purity (UHP) N$_2$ was the carrier gas for each source. During the growth process, mixture of UHP O$_2$, an oxidant, and UHP N$_2$ were introduced into the reactor.
using a separate line. All delivery lines and the inlet flange were wrapped with heating tapes and maintained at 130°C to prevent condensation of the vapor phase precursors. Typical deposition conditions of this experiment are summarized in Table 1.

A Rigaku rotating anode equipped with Huber four-circle diffractometer was employed for X-ray diffraction (XRD). In addition to 0-2θ scans, ω-scans and in-plane Φ scans were performed to observe the degree of mosaic spread and the crystallographic orientation between the films and the substrates.

Cross-sectional transmission electron microscopy (XTEM) samples were prepared by gluing two pieces together with thin films facing each other using M-bond 610. The glued slab was cut into 0.3-mm thicknesses and ground using diamond-lapping films down to 5-8 µm to be ion-milled till they are electron transparent. For plan-view transmission electron microscopy (TEM) samples, bulk samples were ground from substrate side down to 5-8 µm for ion-milling. Two different depths of plan-view images, one from the area at the top of the film and the other close to the interface, were investigated to compare the growth characteristics of an initial stage of the growth and the post competitive growth. A plan-view sample close to the interface was obtained by ion-milling the top surface of the film till the substrate diffraction spots could be observed.

Analytical data were obtained using CM12 for a normal image observation and a VG H501 scanning transmission electron microscope with a 2 nm spot size was used to get energy dispersive X-ray mapping of the elements. High-resolution images were obtained using a Hitachi H9000 microscope at 300 kV and the Fourier transformation was done using the Digital Micrograph version 3.3.

The composition of the samples was determined using a combination of Rutherford backscattering (RBS) and secondary ion mass spectrometry (SIMS, Cameca IMS 5f). First, RBS was performed on one of the samples and a computer simulation program (RUMP) was employed to determine its composition. Once this was done, the sample served as a standard for further analysis using SIMS in a depth profile mode. The relative cation ratio (Ta-to-Sn) was determined for each sample by averaging secondary ion yields in the bulk region. All the concentrations of Ta in this paper is relative concentration presented as a ratio of Sn/(Sn+Ta).

Room temperature dc resistivity was measured using a Van der Pauw geometry. Several currents were applied from 1 µA to 10 mA in one-order increments. The measurement was done as described in an ASTM manual [8]. The carrier concentration was determined by ac Hall measurement under 4.5 T with 0.1 mA (Quantum Design PPMS model).

### 3. Results

Fig. 1a shows 0-2θ scans of samples grown at 400, 500, and 600°C ranging from 25 to 55°. In addition to the strong substrate normal, Al2O3(0006), peak at 41.7°, all films show a major peak that corresponds to SnO2(200) reflection regardless of the growth temperature indicating an out-of-plane orientation of SnO2(100)//Al2O3(0001). There are also other reflections such as (110), (101), and (211), but the intensity of these reflections are small. As the growth temperature increases, the intensity of the SnO2(200) reflections becomes stronger and remaining peaks that belong to other reflections of SnO2 become negligible. This is because at relatively high growth temperature, Sn-atoms have enhanced mobility to a reach stable or equilibrium position on the Al2O3(0001) surface and nucleation occurs of a particular orientation that is preferred, resulting in better structure of the film.

The 2θ position is also a function of the growth temperature. 2θ positions of all of the (200) reflections are close to but different from that of the bulk SnO2(200) reflection for which the 2θ value is 37.98°. This may be due to the strain induced by the lattice mismatch and possibly misplaced adatoms in the lattice due to lack of mobility of adatoms. Interplanar spacing of (1120) planes of Al2O3, \(d_{[1120]}\), is 0.476 nm while that of SnO2, \(d_{[SnO2]}\), is 0.474 nm. Because of the larger lattice spacing of Al2O3, when epitaxy is formed, films will have tensile stress. Interplanar spacing of the films along the growth direction will be smaller than bulk value to maintain the fixed volume of unit cells in epitaxial positions. As the film grows, stress will be accumulated in the film, but the build-up will be partially relieved by dislocations and competitive growth of grains. At higher concentration of Ta, polycrystalline grain boundaries act as another relaxation source. Threading dislocations, not shown here, were observed in all films studied in this paper. We expect reduced interplanar spacing along growth direction as the films have better epitaxial relationship with substrate.

Fig. 1b is a series of XRD 0-2θ scans of SnO2 thin films grown at 600°C with various amounts of Ta-
doping. Except for the film with the highest Ta-doping, all films are oriented with the Al$_2$O$_3$ lattice directions such that the out-of-plane orientation is SnO$_2$(100) // Al$_2$O$_3$(0001) as observed in the undoped film. Interplanar spacing along the growth direction decreased when Ta is added compared with pure SnO$_2$. The 2θ position of the SnO$_2$(200) reflection, 38.28° ± 0.02, does not change with the amount of Ta-doping, but decrease in intensity as the amount of Ta added. The fixed 2θ position with various amounts of Ta is interesting, as shown in aspects of this experiment. When 1.35% of Ta was added, the best epitaxial growth was obtained, then there was gradual decrease in the peak intensity with the amount of Ta. The development of the SnO$_2$(200) reflection at 1.35% Ta-doping shows less Mosaic spread as shown in Fig. 1c that contains ω-rocking curves of (200) reflection. The full width at half max (FWHM) of the undoped and 1.35% Ta-doped film are 1.10° and 0.65°, respectively. The atomic scattering factor also plays a role because Ta has a larger atomic scattering factor than Sn. However, due to the small amount of Ta incorporation, atomic scattering effect is believed to be minimal. With further increase in the Ta doping, the SnO$_2$(200) reflection becomes weaker and broader. Finally, the out-of-plane orientation is no longer observed in the 8.3% Ta-doped film and the XRD pattern is similar to a randomly distributed powder pattern.

Fig. 2 shows the off-specular Φ-scans of Al$_2$O$_3$ {1123} and SnO$_2$ {110} planes of undoped (a) and Ta-doped (b) films. Both Fig. 2a and (b) reveals clear epitaxial relationship between the films and the substrates. The undoped film shows the two distinct in-plane alignments with respect to the substrate. The major peaks are determined with respect to the Al$_2$O$_3$ {1123} reflections, suggesting that SnO$_2$(010) is parallel to Al$_2$O$_3$(1120). The appearance of six-fold-like feature is a combined effect from film and substrate geometry [9]. The Al$_2$O$_3$(0001) surface has six equivalent directions that allow the growth of SnO$_2$(100) to follow the substrate geometry. Among these six directions, only three of them are distinguishable. More interestingly, another set of SnO$_2$(110) reflections separated by 60° from the major ones and also 60° apart from one another was observed. Once the Ta was introduced, the secondary set of reflections disappeared as seen in Fig. 2b.
density of dislocations. In both types of grains, twins are observed with twin plane of SnO$_2$[101]. It is observed that SnO$_2$[100] zone axis of dislocation-free large grains is tilted $\sim 10^\circ$ from the growth plane normal, which might be contributed by the part of strain relaxation. Most of the small grains have a crystallographic orientation of SnO$_2$(100)/Al$_2$O$_3$(0001) with SnO$_2$[100]/Al$_2$O$_3$(1120). Some of weak diffractions are also observed at the top of the film and close to the interface, which have an in-plane crystallographic orientation of SnO$_2$(100)/Al$_2$O$_3$(0001) with SnO$_2$[010]/Al$_2$O$_3$(1120). These results are in good agreement with the relationship obtained by the in-plane XRD $\Phi$-scan shown in Fig. 2. The grains with the latter relationship are not always nucleated at the triple point as an entrapped form. The population ratio of the grains with the epitaxial relationship of SnO$_2$[010]/Al$_2$O$_3$(1100) to the grains with the epitaxial relationship of SnO$_2$[100]/Al$_2$O$_3$(1120) is estimated as 0.23±0.04 from the area count obtained from dark field images. This is also in agreement with the in-plane XRD $\Phi$-scan measurement. The ratio of the integrated intensity of the peaks corresponding to SnO$_2$[010]/Al$_2$O$_3$(1100) to SnO$_2$[100]/Al$_2$O$_3$(1120) is approximately 0.20 obtained by Gaussian fitting of each reflection in XRD.

Even though the competitive growth governs throughout the thickness of the film, the degree of crystallographic orientation stays the same from the interface to the top of the film. To verify the initial stage of growth of the grains with SnO$_2$(100)/Al$_2$O$_3$(0001) and SnO$_2$[010]/Al$_2$O$_3$(1100), high-resolution images were taken from an area of Fig. 3b including both the substrate and the film. Fig. 4 shows a high-resolution image and the corresponding Fourier transformed images, a–e, taken from the different areas of high-resolution images. Location A is from the substrate showing Al$_2$O$_3$(0001) image, where the corresponding reconstructed diffraction pattern is shown as a in the Figure. The area marked as B represents the epitaxial relationship of SnO$_2$[010]/Al$_2$O$_3$(1100) overlaid with Al$_2$O$_3$(0001) zone with the corresponding diffraction pattern shown as b. Areas marked as C, D, and E are from the grains with the epitaxial relationship of SnO$_2$[100]/Al$_2$O$_3$(1120). Corresponding reconstructed diffraction patterns from Fourier transformations from the marked area are also shown as c, d, and e. It is clear to observe the existence of the grains with two distinct epitaxial relationships as well as the degree of the epitaxy. The nature of the epitaxy is determined at the initial stage of the growth.

Fig. 5 shows a similar configuration of XTEM and plan-view images of 1.35% Ta-doped film. Both XTEM and plan-view images show nearly same microstructure as undoped film, but the SAEDs clearly show the difference. The top of the film has the same level of the
rotation of grains, and clean grains from competitive grain growth. Diffraction patterns have a clear epitaxial relationship with sharper spotty patterns. The additional diffraction patterns that was belonged to the orientation of $\text{SnO}_2[010]/\text{Al}_2\text{O}_3(1100)$ are no longer visible, which was confirmed by in-plane XRD $\Phi$-scans.

Fig. 6 shows the change of the electrical resistivity, carrier concentration, and mobility as a function of Ta concentration, which was presented as a ratio of Sn/(Sn + Ta). The electrical resistivity of the films varied from 0.1 to $2\times10^{-3}$ $\Omega$ cm with a minimum of $3.1\times10^{-4}$ $\Omega$ cm at 1.35% Ta-doping. Ta concentration strongly affects the resistivity change in the films with less than 1.35% Ta-doping. The resistivity slowly increases with concentration in the films with more than 1.35% Ta-doping but the change is not distinct as in lower concentrations of Ta. Saturation of resistivity curve may be attributed to the lattice scattering effect when the film lose epitaxially grown grains and the change in the ionic charge states.

4. Discussion

A new epitaxial relationship of undoped SnO$_2$ film on Al$_2$O$_3$(0001) substrate, SnO$_2$(100)/$\text{Al}_2\text{O}_3$(0001) with SnO$_2$(010)/$\text{Al}_2\text{O}_3$(1100), is observed in this study and a possible geometry is constructed in Fig. 7 along with the previous proposed atomic arrangement [7]. A rectangle formed by the SnO$_2$(100) plane is drawn utilizing existing Al and deposited Sn atoms. Once this SnO$_2$(100) plane is set, oxygen atoms follow the hexagonal-closed-packed (hcp) arrangement and the crystal growth proceeds. Because of the surface structure of Al$_2$O$_3$(0001) surface with the two-fold symmetry of SnO$_2$(100) plane, the six-fold-like feature is also observed. However, the in-plane alignments of SnO$_2$(100) planes according to SnO$_2$(010)/$\text{Al}_2\text{O}_3$(1100) is no longer visible, which was confirmed by in-plane XRD $\Phi$-scans.
that the affinity and mobility of adatoms with surface atoms are the critical factors setting up seeds for further growth. High temperature growth can provide higher mobility of adatoms, which can find more stable positions compared to the ones grown in low temperature. The absence of the secondary orientation seems to be related to the reactivity of Ta toward oxygen atoms. As shown in Fig. 7, oxygen atoms in the first SnO$_2$(400) layer does not exactly follow the hcp arrangement of the Al$_2$O$_3$(0001) surface. Once Ta is introduced, it is substituted into Sn atom sites and there would be a greater attraction toward the oxygen atoms. Lattice parameters of (Sn+Ta)O$_2$ increases compared to the undoped film because the ionic radius of Ta is larger than Sn [10]. By adding up to a certain level of Ta to existing SnO$_2$ lattice, it can provide favorable condition in lattice-mismatched system of SnO$_2$ on Al$_2$O$_3$ because of the larger ionic diameter of Ta. Ta atoms also have more affinity than Sn atoms to oxygen [10]. However, the addition of excessive Ta atoms can fill the energetically unfavorable sites for Sn and oxygen atoms to form bonds for epitaxial growth. Reduction of SnO$_2$(200) peak intensity in Fig. 2b can be explained as the breakdown of favorable conditions for epitaxial growth from the excessive Ta.

An addition of Ta into SnO$_2$ lowered the electrical resistivity by three orders of magnitude. The increase in the charge carrier concentration is the most influential factor for the decrease in the resistivity. The carrier concentrations in 1.35 and 4.02% Ta-doped film are approximately $4.7 \times 10^{20}$ and $1.34 \times 10^{21}$/cm$^3$, respectively.

Besides the increase in the charge carriers, an appreciable enhancement of the mobility, 42.9 cm$^2$/Vs, was also observed at room temperature in the 1.35% Ta-doped film, indicating that the change in the resistivity is also closely related to the microstructural improvement. Improvement of mobility is believed to come from the lattice plane alignment with less mosaicity of grains. As a result, the scattering of electrons is reduced at grain boundaries and also in adjacent lattice planes.

In summary, a new crystallographic orientation of SnO$_2$(010)/Al$_2$O$_3$(1100) observed when undoped SnO$_2$ was grown on Al$_2$O$_3$(0001). A value of 1.35% Ta addition is the optimum condition for the electrical characteristics to be used in the transparent conductor. We believe this system can be a potent candidate for the next generation transparent conductor.

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References