Research Article

Effect of the Change of Deposition Time on the Secondary Direction and Abnormal Shape of Grains Growth of SnO_2 Thin Films

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SnO_2 thin films were grown on Si substrate using the low pressure chemical vapor deposition method. Observations made through electron microscopy indicate that thin films tend to grow with a constant direction when deposited at a temperature of 420°C for 5, 10, 20, or 30 min. However, when the deposition time increases, the particles forming the thin films are subject to a secondary growth. Observations made under a high-resolution transmission electron microscope reveal the lattice shape characteristic of thin films, with an overlapped or wrinkled flower form, and indicate that thin films growth takes place in different directions during the secondary growth. Measurements of the Hall effect show that the carriers mobility in the thin films increases linearly with the deposition time, whereas the carrier density decreases. The Hall R_h value increased linearly until 20 min deposition time, whereas for thin film grown for 30 min it decreased rapidly, showing a relatively similar behaviour to the carrier density. This is because as the deposition time becomes longer, the second growth and atypical shape occurs, leading to an increase of the thin films R_h value. This phenomenon indicates that the deposition time of thin films affects their carrier density and atypical overlapped or wrinkled flower form.

1. Introduction

The chemical vapour deposition (CVD) method is based on the growth of thin films through the chemical reaction of a precursor gas with the substrate surface, which usually takes place because of the movement of the reactants due to convection, diffusion, absorption on the surface of the substrate, or expansion of the by-products generated during the reaction. In case of SnO_2 thin films deposited through CVD, specific factors may affect the growth, including the deposition temperature and time, the amount of precursor material, the amount of added oxygen, and the level of vacuum in the chamber [1, 2]. The nucleation initiates when the reactants reach the substrate, thanks to the diffusion mechanism, and are adsorbed on its surface. When the formed nuclei have a critical size, they start growing and thin films are formed. Deposition of thin films derives from the chemical reaction between vapour originating from the substrate surface and vapour coming from the precursor gas,

so it can be considered to be a chemical reaction produced by a solid state. The eventual by-products of the described surface reaction originate by desorption from the substrate surface and are eliminated after expansion of the surface over the original boundaries. Because of the effect of the surrounding environment on the deposition conditions, thin films grow with different morphologies [3–6]. Additionally, since thin films grow thicker as the deposition time increases, their structural and electrical characteristics change. Table 1 shows deposited condition of thin films.

2. Experiment

SnO_2 thin films were grown using CVD. The precursor material was dibutyltin diacetate (DBT, Sigma-Aldrich, purity 99.99%) and was transported by argon (Ar) gas and then evaporated on to the films by oxygen (O_2) flowing into the chamber. A Si wafer was used as the substrate; Si substrate has

TABLE 1: Deposition conditions for SnO₂ thin films.

Sample	Deposition time (min)	Deposition temperature (°C)	Gas flow rate Ar: O (sccm)
420-5	5	420	10 : 10
420-10	10	420	10 : 10
420-20	20	420	10 : 10
420-30	30	420	10 : 10

been washed initially for 10 s in acetone solution followed by pure water and exposed in spilled nitrogen gas in the vacuum state. The deposition temperatures of the thin film were 420°C, with a deposition time of 5, 10, 20, and 30 minutes. The inflow rate of oxygen was set at 10 sccm to fabricate the SnO₂ thin film. The surface of the deposited SnO₂ thin films could be observed using scanning electron microscopy (SEM; Hitachi, S-4700, Japan), and transmission electron microscopy (TEM; Technai, F20, Phillips, Netherlands) was needed to observe the thin film, by the electron density penetrating through the layer with an electron beam emitted with 200 kV. An image analyzer was used to measure the sizes of particles and the thickness of the cross section. The Hall coefficient was calculated by applying the van der Pauw method.

3. Results and Discussion

Figure 1(a) shows the surface morphology of SnO₂ thin films grown for 5 min at a deposition temperature of 420°C. They present a uniform morphology, with grains having a size ranging between 0.01 and 0.16 μm on their main axis, and an average size of 0.1 μm . Figure 1(b) shows the surface morphology of thin films grown for 10 min at 420°C. They present a uniform morphology, with grains having a size ranging between 0.01 and 0.16 μm on their main axis, and an average size of 0.1 μm . Figure 1(c) shows the surface morphology of SnO₂ thin films grown for 20 min at a deposition temperature of 420°C. They present grains with a size ranging between 0.01 and 0.2 μm on their main axis and an average size of 0.11 μm . Figure 1(d) shows a scanning electron microscope image of the surface morphology of SnO₂ thin films grown for 30 min at 420°C. They present grains with a size ranging between 0.01 and 0.22 μm on their main axis, although their average size was 0.15 μm .

The thin films were more dense and there were new particles in comparison with the thin films grown for 10 or 20 min. As explained above, the growth of thin films starts from a nucleation process: when the nuclei reach a critical size, the grains grow rapidly and an additional growth appears. This additional growth may affect the direction and the velocity of thin films formation.

In the CVD equipment, oxygen gas flowed into the chamber in a gaseous state. Then, starting material (DBT) in the canister vaporized in a liquid state. As a result, we considered that the SiO₂ layer was deposited in the early stage by reacting oxygen gas with Si substrate, and then the SnO₂ layer was deposited [7]. The thickness of the SiO₂

layer may affect the growth of SnO₂ thin films particles [8]. The growth of SnO₂ thin films may depend also on the deposition temperature and time, on the amount of added oxygen, and on the amount of the transport gas [9]. The relatively short deposition time generates a constant growth of particles; nonetheless, when the deposition time becomes more prolonged, the thin films density increases and new particles appear. In order to confirm this phenomenon, high-resolution transmission electron microscopy was used to study thin films formed at 420°C deposition temperature for 30 min. TEM sample was prepared by using Focus Ion Beam (FIB) through the process of beam deposition, tilting cutting, and side cutting and milling. Figure 2 shows the transmission electron microscopy for 420°C, 30 min of SnO₂ thin films. Atomic scale images of the thin films were obtained by field emission TEM at 200 kV. It shows most of SnO₂ thin films particle grow in the same direction.

However, when selected areas (around 2 nm) of Figure 2(b) are observed with a higher magnification (see white marks), it appears that SnO₂ thin films grow in various directions and many wrinkles are formed, proving that the evaporation is not progressing equally. As shown in the picture, most of the thin films grew in one direction; yet, in selected areas (pointed by the white marks), since the layers generating the thin films were overlapped and the deposition was longer, the particles forming the thin films grew in different directions, similar to crossed stripes. This is evident also in Figure 1(d) which also shows that, on the surface of thin films, among the bigger particles, small particles grow overlapped on each other. As mentioned above, SnO₂ thin films grow differently according to their deposition conditions [10]. The main factors affecting the growth of thin films by CVD are the temperature, the deposition time, the type of precursor, the amount of added oxygen, and the level of vacuum in the chamber. The most important factor affecting the growth of thin films, among the ones mentioned above, is the stability of the vacuum in the chamber. If the vacuum level is unstable or the original surface swells due to the formation of an oxygen layer, the SnO₂ thin films particles may assume a disordered structure. When a crystal forms, first the nucleus is generated, and then the adjacent atoms or ions stick to the nucleus in a preferential order determined by the energy level of the lattice, forming a regular layer; on the other hand, if the growth occurs continuously, the particles may expand in two dimensions and overlapping of the particles may occur. Therefore, thin films may present a different lattice pattern compared to the previous one, and this might be due to a reduced density of thin films.

Figure 3 shows TEM micrographs of films grown for 30 min at 420°C. Figure 3(a) shows most of SnO₂ thin films cross section grows in the same columnar direction. Some parts of the cross section were atypical shape occurred. The high-resolution TEM microstructure embedded in Figure 3(a) showed the flower shape. However, when selected areas (around 200 nm) of Figure 3(b) are observed with a higher magnification (see white marks), it appears that SnO₂ thin films grown in wrinkled flower are formed. In the previous reports the SnO₂ particle growth formation shows

FIGURE 1: SEM micrographs of SnO_2 thin films grown at 420°C for (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min.

FIGURE 2: TEM micrographs showing the surface morphology of SnO_2 thin films for 20 nm (a) and 2 nm (b), respectively.

atypical growth in various conditions. This is the secondary growth of the thin film with atypical particle form which has high electrical resistance. Therefore, we could expect the facial electrical resistance of a film with uniform-grain shape of the particles to have a significant relation with the thin film surface structure.

Figure 4 shows the data relative to the Hall effect measured for thin films grown at 420°C for 5, 10, 20, and 30 min. As the deposition time increased, also the resistance of thin films increased. As thin films became thicker their electrical resistance increased, and, as a result, electrical resistance value at inside of the thin films will increase. Also, the carrier

FIGURE 3: TEM micrographs showing the cross section morphology of SnO_2 thin films for 1 μm (a) and 200 nm (b), respectively.

FIGURE 4: Hall data of SnO_2 thin films.

mobility in the thin films increased linearly as the deposition time increased. The oxygen vacancies may appear, due to defects or to the presence of an interface inside the SnO_2 thin films, affecting the carrier mobility in the formed films. As the thin films deposition time increased from 5 to 20 min, the carrier density decreased linearly; however, at 30 min of deposition time the carrier density decreased more rapidly. SnO_2 thin films are n-type semiconductors, and the change in the carrier density is due to oxygen vacancies generated during thin film growth [11]. The carrier density tended to decrease as the deposition time increased. It was further examined, the SnO_2 grains were relatively closely distributed on the surface, and the carrier density was low because they grew along the densest plane of the rutile structure. The deposition time increased, the crystal growth direction of the surface became disordered, and more surface area was exposed to air. Moreover, the oxygen vacancy concentration decreased rapidly, and the electric resistance of the thin film

increased because many SnO_2 grains that did not satisfy the stoichiometric composition were distributed. The R_h value increased linearly until 20 min deposition time, whereas for thin film grown for 30 min it increased rapidly, showing a relatively similar behaviour to the carrier density. This is because as the deposition time becomes longer, the second growth and atypical shape occurs, leading to an increase of the thin films R_h value. As the thin films R_h value increases, the defects or the oxygen vacancies inside the films decrease with respect to their surface. Thus, when the deposition time increases, the carrier density decreases, due to the formation of oxygen vacancies or defects inside the thin films. For sensors or other electronic applications based on SnO_2 thin films, it is necessary to consider the electronic changes associated with the second growth occurring in the thin films.

4. Conclusions

When the deposition time is increased, a secondary growth occurs in the thin films; the overlapping crossed stripes mentioned above or a wrinkled morphology would then take place on the inner side of the thin films. SnO_2 thin films cross section grows in the same columnar direction. Some parts of the cross section were atypical wrinkled flower shape occurred. This phenomenon changes the oxygen vacancies distribution by modifying the density or the defects inside the thin films. In addition, it changes the electronic characteristics of the thin films by altering their carrier density.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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