Effect of Mg doping on optical and electrical properties of SnO$_2$ thin films: An experiment and first-principles study

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Abstract

Transparent Mg-doped p-type conductive SnO$_2$ thin films were fabricated on quartz substrates by sol–gel method. Effect of Mg doping on structural, morphological, optical, and electrical properties of SnO$_2$ films were investigated. A single phase of tetragonal rutile structure was observed in Mg-doped SnO$_2$ films. The optical bandgap energy of the Mg-doped SnO$_2$ films showed a systematical redshift with respect to the undoped SnO$_2$ film, and the resistivity significantly increased with the increase of Mg concentration. A conduction type transform from n to p was also observed. The strong ultraviolet and comparatively weak blue/green emissions were observed in room temperature photoluminescence, suggesting the dipole-forbidden rule of bulk SnO$_2$ is broken in Mg-doped SnO$_2$ films. These results were supported by first-principles electronic structure calculations.

1. Introduction

Even after few decades of intense research on the wide-bandgap oxide semiconductor, stannic oxide (SnO$_2$) remains a very active material for research up to now [1–6] SnO$_2$ has a wide direct bandgap of ∼3.6 eV, is extensively applied in the fields of gap sensors, solar cells, high performance capacitor and so on due to its excellent optical and electrical properties [7–14]. However, the following characters of undoped bulk SnO$_2$ hinders its further application in the optoelectronic field: (i) Bulk SnO$_2$ cannot attain efficient ultraviolet (UV) emission due to the dipole-forbidden rule [15–17]. (ii) Undoped SnO$_2$ usually shows strong n-type conduction and the lack of p-type conduction [18]. To recover the optical activity of SnO$_2$ and realize the UV emission, some researchers utilized nanoengineering and doping methods to modify SnO$_2$ electronic structure so that the dipole forbidden rule can be broken [15,16]. In order to obtain p-type SnO$_2$, some metal ions as acceptor impurities are expected to play an important role in producing the p-type conductivity and improving the efficiency of photoluminescence (PL). Meanwhile, different fabrication methods that can be used to produce p-type SnO$_2$ films including reactive sputtering [19], chemical vapor deposition [20], dip coating [21], evaporation, spray pyrolysis [22] and sol–gel [15,23]. Among these methods, sol–gel method can produce dense thin films with the least expensive and lower processing temperature [23]. Actually, some researchers have claimed that SnO$_2$ could exhibit a p-type behavior when doped with metal elements such as Al, In, Sb, Zn and Ga [24–26]. Nevertheless, to our knowledge, there have been no or little efforts reported on the structure, p-type

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conductivity and optical properties of Mg-doped SnO_2 (SnO_2: Mg) thin films grown on quartz substrate by sol–gel process.

In this paper, Mg-doped SnO_2 thin films with different Mg concentration were fabricated on quartz substrates. The effect of Mg doping on the structural, optical, and electrical properties of the Mg-doped SnO_2 thin films were investigated in detail.

2. Experimental and first-principles calculations details

The undoped and Mg-doped SnO_2 thin films were synthesized on quartz substrates using the sol−gel method. The tin chloride pentahydrate ($SnCl_2 \cdot 2H_2O$) and magnesium chloride ($MgCl_2 \cdot 6H_2O$) were used as precursors for preparing the SnO_2:Mg thin films. First, to prepare the sol solution, $SnCl_2 \cdot 2H_2O$ were mixed into 10 mL of ethanol and stirred using a magnetic stirrer for 1 h at 80 °C. The different amount of $MgCl_2 \cdot 6H_2O$ was also hydrolyzed in ethanol (10 mL) and stirred for 3 h. Then, the two presolutions were mixed together, after that the mixed liquid was spin-coated on clean quartz substrates. After spin-coating, the films were baked at 180 °C for 5 min. Finally, the films were annealed under air ambient in a horizontal quartz-tube furnace at 900 °C for 1 h.

For structural characterizations, x-ray diffraction (XRD) was carried out using a powder diffractometer with a Cu Kα radiation. The optical absorption spectra were recorded using an UV−visible−near infrared spectrophotometer. The room temperature PL measurements were performed using a He–Cd laser with a 325 nm line as the excitation source. The electrical properties of the films were measured using a Hall Effect equipment with van der Pauw configuration. The surface morphology of the thin films was examined by using a scanning electron microscopy (SEM, Hitachi S-4800).

First-principles calculations were carried out using the CASTEP code within a framework of density functional theory (DFT) in generalized gradient approximation (GGA) and ultrasoft pseudopotentials [27]. For the Sn atoms, d states were treated as valence states. We constructed a 72-atom $2 \times 2 \times 3$ SnO_2 supercell with the rutile structure. To simulate the Mg-doped SnO_2, a Sn atom is substituted by a Mg atom. The cutoff energy for the plane-wave basis set is 500 eV. In the calculations, all the atoms are allowed to relax until the Hellmann−Feynman forces acting on them become less than 0.01 eV/Å. The optimized a- and c-axis lattice constants of perfect SnO_2 are 4.772 and 3.233 Å with a small error of 0.7% and 1.5% with respect to the experimental values. For k-points sampling, a $2 \times 2 \times 2$ Monkhorst–Pack mesh in the Brillouin zone was used. To simulate the optical properties of the polycrystalline SnO_2, the polarized absorption from x-, y- and z-direction is averaged. Although the calculated bandgap of pure SnO_2 is underestimated with respect to the experimental value, it does not affect our discussion on the results.

3. Results and discussion

Fig. 1 shows the XRD patterns of undoped SnO_2 and SnO_2: Mg thin films deposited for different Mg concentrations.
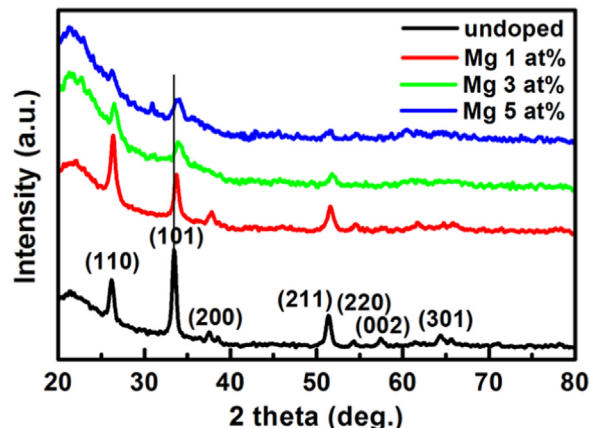

Fig. 1. XRD patterns of the undoped and Mg-doped SnO_2 thin films deposited on quartz substrates.

Besides the broad band at 20–25° deriving from the amorphous quartz substrates, the peaks corresponding to diffraction planes (110), (101), (200), (211), (220), (002), and (301) of SnO_2 are observed, which is in agreement with the standard JCPDS data (File no. 41-1445). This observation indicates that the films have polycrystalline nature with rutile structure. No second phase related to Mg dopants is observed, suggesting that Mg was incorporated into the SnO_2 lattice. The (101) diffraction peak shifts to larger angle as Mg concentration increases, indicating a lattice shrink due to smaller Mg^{2+} ionic size than Sn^{4+} (0.067 nm versus 0.071 nm) [15,28]. The broadening of the diffraction peaks increases gradually with an increase in Mg doping level, indicating that its crystalline structure tends to be deteriorated. Similar results were also found in Al-doped SnO_2 films [25].

The optical absorption spectra of the samples with various doping concentrations are shown in Fig. 2. By extrapolation of the linear part of the curve, the intersection with energy axis determines the bandgap [29]. It is found that the bandgap of undoped SnO_2 is 3.77 eV, which is slightly larger than the typical value of bulk SnO_2 (3.6 eV). The obtained values of the optical bandgaps are 3.73, 3.60, and 3.50 eV, respectively, for the SnO_2:Mg films with Mg concentrations of 1, 3 and 5 at%, as shown in the insert of Fig. 2. Generally, bandgap of n-type semiconductor increases while doping with donors, or decreases on acceptor doping [28,30,31]. Mg substitution in Sn site may create two holes because of lower valence state of Mg^{2+} ion as compared to Sn^{4+} ion. This is in accord with the previous results from by Shjira et al. [30]. Acceptor doping inducing the decrease of the bandgap is attributed to the acceptor state in the gap and the compensation of intrinsic donor to acceptor and the formation of impurity band.

Fig. 3 shows the SEM images of the undoped and Mg-doped SnO_2 thin films. These films are found to be uniform. The surface morphology of the films is strongly dependent upon the Mg concentration. The undoped SnO_2 films revealed roughly a homogenous surface consisting of crystallites. It can be seen that the surface of the SnO_2:Mg thin films consist of homogeneous nano-sized grains. The mean grain size increases with increasing Mg concentration.