



# Giant enhancement of ultraviolet near-band-edge emission from a wide-bandgap oxide with dipole-forbidden bandgap transition



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## ABSTRACT

We report giant enhancement of recovered ultraviolet near-band-edge emission from SnO<sub>2</sub> thin films with dipole-forbidden bandgap transition via Ag-doping and surface plasmon coupling. It is found that a recovering near-band-edge emission in the range of 361–375 nm in a low-concentration Ag-doped SnO<sub>2</sub> film, suggesting that dipole-forbidden transition rule of SnO<sub>2</sub> is broken. First-principles electronic structure calculations indicate that the breaking of the dipole-forbidden transition rule is derived from the acceptor of Ag substituting Sn in SnO<sub>2</sub>. 30-fold enhancement of ultraviolet near-band-edge emission from the Ag-doped SnO<sub>2</sub> film is observed by modifying film surface using Ag nanoparticles. The giant enhancement of ultraviolet emission is ascribed to surface plasmon coupling between Ag-doped SnO<sub>2</sub> and Ag nanoparticles. Our results suggest that Ag doping and Ag nanoparticles surface modification in SnO<sub>2</sub> films play important roles in recovering and enhancing ultraviolet emission of SnO<sub>2</sub> with dipole-forbidden bandgap transition.

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## 1. Introduction

Wide-bandgap oxides have attracted much attention due to their rich functionalities and technological applications [1–11]. Among these oxides, tin dioxide (SnO<sub>2</sub>), as a wide bandgap semiconductor, has been applied in the fields of transparent conducting thin films, solar cells, gas sensors, catalysis and so on [12–18]. Although bulk SnO<sub>2</sub> has a wide direct bandgap of ~3.6 eV, it cannot efficiently emit ultraviolet (UV) light due to the dipole-forbidden nature of its band edge quantum states [19], which has hindered its potential use in optoelectronic applications, such as photodetectors and light-emitting diodes (LEDs). In our previous work, to recover the optical activity of SnO<sub>2</sub> and realize the UV near-band-edge (NBE) emission, we utilized nanoengineering and doping engineering to modify SnO<sub>2</sub> electronic structure so that the

dipole-forbidden rule can be broken and we also demonstrated SnO<sub>2</sub>-based UV LEDs [12,13]. However, the intensity of UV emission from the SnO<sub>2</sub> layer is still weak. Recent decade, Surface plasmons (SPs) have been widely used to improve the emission efficiency of light emitting materials and devices [20]. For instance, Okamoto. *et al* reported the SPs enhanced light emitters based on InGaN quantum wells [21]. To achieve enhancement of UV emission induced by SPs, one of key factors is the energy match. The exciton energy can be rapidly transferred to plasmon excitation when the large frequency overlaps between SPs electric field and semiconductors [22,23]. Therefore, the key to enhance the UV emission is to choose the appropriate metal. Grontijo *et al.* reported that the first example of resonance coupling of the semiconductor spontaneous emission into SPs [24]. For metal Ag, the bulk plasmon energy is 3.7 eV and the SPs energy is somewhat lower, depending on the retroactive index of the adjacent dielectric [25–27]. The result indicates that this energy range is fortunate since the SnO<sub>2</sub> can be resonant with Ag SPs. Hence, the feature of the Ag surface plasmon resonance (SPR) effect can be also applied to the field of SnO<sub>2</sub> thin films to enhance the UV emission. To the best of our knowledge,

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there has been no report on enhancement of the UV emission in SnO<sub>2</sub> thin films.

In this paper, we demonstrate the recovering UV emission in the SnO<sub>2</sub> thin film with dipole-forbidden bandgap transition via Ag-doping and the UV giant enhancement induced by SPR effect in the Ag-doped SnO<sub>2</sub> film with surface modification using Ag nanoparticles (SnO<sub>2</sub>:Ag/Ag nanoparticles hybrid films).

## 2. Experimental process and first-principles calculations detail

The SnO<sub>2</sub>:Ag/Ag nanoparticles hybrid films were synthesized on quartz substrates using the sol-gel method. Fig. 1 shows the schematic synthesization process of the SnO<sub>2</sub>:Ag/Ag nanoparticles hybrid films. An undoped SnO<sub>2</sub> layer was first deposited on quartz substrates by sol-gel method. The detailed synthesization method of the undoped SnO<sub>2</sub> layer can be found in our previous work [13]. Then a layer of silver nitrate (AgNO<sub>3</sub>) sol was spin-coating on the undoped SnO<sub>2</sub> layer. Finally, the films were annealed in a horizontal quartz-tube furnace exposed in the air at 500 °C for 1 h to obtain the SnO<sub>2</sub>:Ag/Ag nanoparticles hybrid films. The Ag concentration in the hybrid film can be controlled by changing AgNO<sub>3</sub> concentration in the sol. Four samples with various Ag concentration were obtained and are denoted as T0, T1, T2 and T3, corresponding to Ag concentration of 0, 0.5 at.%, 1 at.% and 2 at.%, respectively.

X-ray diffraction (XRD) measurements were carried out for structural characterization using a powder diffract meter with a Cu K $\alpha$  radiation. The optical absorption measurements were performed using a UV–vis–near-IR spectrophotometer. The morphologies of the samples were characterized by using scanning electron microscope (SEM). A transmission electron microscope (TEM) was used to examine the crystalline structure of the samples. The photoluminescence (PL) measurements were performed using a He–Cd laser with a 325-nm line as the excitation source. The chemical states of Ag in the hybrid films were detected using x-ray photoelectron spectroscopy (XPS) with Al K $\alpha$  ( $h\nu = 1486.6$  eV) x-ray radiation source.

First-principles calculations were performed using the VASP code with the projector augmented wave (PAW) method within the frame of density function theory (DFT) [28–31]. All calculations were carried out using the hybrid functional as proposed by Heyd,

Scuseria, and Ernzerhof (HSE) [32,33]. The *d* electrons of Sn and Ag atoms were treated as valence electrons. A 72-atom  $2 \times 2 \times 3$  SnO<sub>2</sub> supercell with the rutile structure was constructed. To simulate Ag doping in SnO<sub>2</sub>, a Sn atom is replaced by an Ag atom in the supercell. The cutoff energy for the plane-wave basis set is 400 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. Although the calculated bandgap of pure SnO<sub>2</sub> is underestimated within HSE framework (2.77 eV), i.e. smaller than the experimental value [12], it does not affect our discussion on the results.

## 3. Results and discussion

Fig. 2a shows the XRD patterns of all samples grown on quartz substrates. It is found that all the thin films are polycrystalline with rutile structure. For the SnO<sub>2</sub>:Ag film with 0.5 at.% Ag concentration (sample T1), no diffraction peak of metal Ag or Ag related phase is observed, indicating that the Ag atoms are doped into SnO<sub>2</sub>. As increasing Ag concentration (>0.5 at.%, T2 and T3), the diffraction peaks of metallic Ag are observed, implying existence of metal Ag phase in the films. In order to further check the existence of metal Ag in the SnO<sub>2</sub> films, XPS measurements were carried out. Fig. 2b shows the Ag 3d XPS spectra of the 2.0 at.% Ag-doped SnO<sub>2</sub> film (T3) before and after its surface was etched by Ar ion. Before etching, there is a strong peak and a weak shoulder for both Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, respectively. The strong peak is attributed to Ag<sup>+</sup> and the weak shoulder to Ag<sup>0</sup> [34,35]. The fitting peaks are located at 367.9, 368.8, 373.9 and 374.8 eV, which is corresponding to Ag<sup>+</sup> 3d<sub>5/2</sub>, Ag<sup>0</sup> 3d<sub>5/2</sub>, Ag<sup>+</sup> 3d<sub>3/2</sub> and Ag<sup>0</sup> 3d<sub>3/2</sub>, respectively. After etching, the intensity of the shoulder is significantly decreases, indicating that metal Ag composition is reduced. The XPS results suggest that the Ag<sup>+</sup> ions, as acceptor dopants, are derived from the Sn sites in SnO<sub>2</sub> and the metal Ag<sup>0</sup> mainly exists on the surface of the SnO<sub>2</sub> films. Fig. 2c shows the SEM image of the 2.0 at.% Ag-doped SnO<sub>2</sub> thin films. It is observed that the ball-shaped Ag particles are scattered on the surface of SnO<sub>2</sub> thin films. The grain sizes of Ag particles are in the range of 300–500 nm, indicating that the size of Ag particles is in nanoscales. A cross-sectional TEM image of the Ag-doped SnO<sub>2</sub> thin films with Ag concentration of 2 at.% is shown in Fig. 2d. A sharp interface between the crystalline film and amorphous substrate is observed.

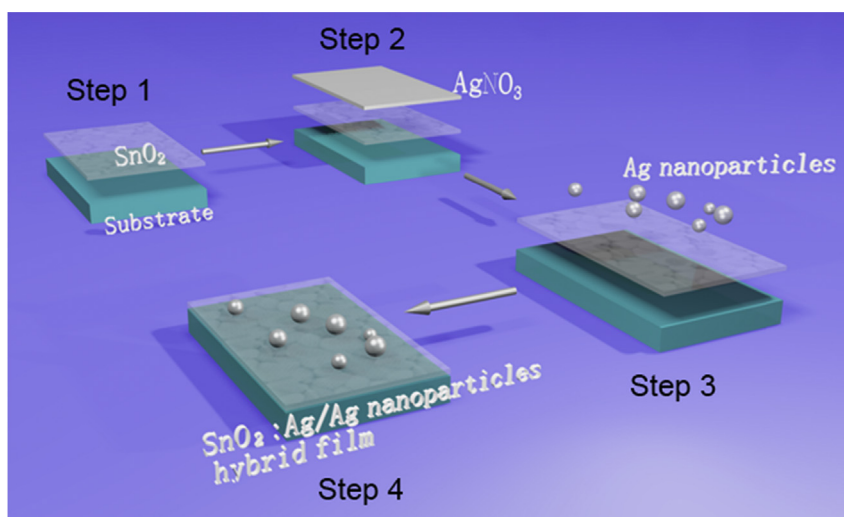


Fig. 1. Schematic fabrication process of the Ag-doped SnO<sub>2</sub> hybrid thin films with Ag nanoparticles surface modification.

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