

Preparation and photoluminescence of TiO₂/PS composite system

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A TiO₂/porous silicon (PS) composite system is prepared by chemical vapor deposition. The crystal form with anatase phase of the samples is evaluated by X-ray diffraction and ultraviolet-visible (UV-vis) absorbance spectra, and the morphology with microsphere of TiO₂ particles is characterized by scanning electron microscopy. The composite system formed by this technique gives a broad blue luminescence and the mechanism of photoluminescence with TiO₂/PS is also discussed.

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Porous silicon (PS) has been studied widely because of its property of visible room-temperature photoluminescence (PL) for possible all-Si-based optoelectronic applications^[1]. However, PS shows unstable PL properties attributed to the instability of the Si-H bonds on the PS surface that gradually break in air^[2]. Therefore, luminescence intensity and stability from PS must be improved for making PS-based photoelectronic integration commercial, especially blue luminescence devices.

Many techniques have been found to improve the efficiency and stability of PL from PS. One of the major techniques is PS compound with other different material systems, for example, ZnO/PS^[3], ZnS/PS^[4], and GaN/PS^[5] have been studied. Kim *et al.* have reported the stable PL of PS at 570 nm by depositing TiO₂ thin film on PS using a method of anodic oxidative hydrolysis, which can be attributed to the TiO₂ passivation^[6]. However, the composite film they prepared did not show blue emitting.

In this letter, a TiO₂/PS composite system is prepared by chemical vapor deposition (CVD) which is a common technique in preparation of nano-materials^[7]. The specimen formed by this technique gives a broad blue luminescence, indicating that the composition is significant to develop blue-light-emitting devices in the field of Si-based optoelectronic systems. Furthermore, TiO₂ has attracted a great deal of attention due to its physicochemical properties and applications in anticorrosion, self-cleaning coatings, optics, and gas sensors^[8–10]. Especially, nano-crystalline TiO₂ films such as TiO₂ nanocomposite microspheres have been the subject of wide attention because of their unusual optical and electrical properties^[9–12]. However, no nanostructured TiO₂ prepared using PS as a template has been reported, though PS is a good candidate as a template due to its unique structure. Therefore, this investigation would be helpful in preparation of nanostructured TiO₂ materials.

The PS samples were prepared by electrochemical an-

odization from (100) oriented phosphorous doped n-type c-Si wafers with a resistivity of 3 – 6 Ω·cm at room temperature. The anodization was carried out in a mixture of ethanol (98%) and HF (49%) (volume ratio of 2:1) at the current density of 30 mA/cm² and the etching time was 20 min. Then, we cut the PS sample into two pieces. One was used as substrate for the deposition of TiO₂ films and the other was used for comparison without any treatment. TiO₂ films have been deposited by CVD technique, employing TiCl₄ and H₂O as Ti and O sources, respectively. For comparison, n-type Si (100) was used as substrate for depositing the same films. The furnace was heated to 900 °C for 30 min and subsequently cooled to room temperature naturally.

The synthesized sample was studied by energy dispersion spectroscopy (EDS), scanning electron microscopy (SEM) using a LEO-1430VP electron microscope, and X-ray diffraction (XRD) using M18XHF22-SRA with Cu-Kα radiation. The ultraviolet-visible (UV-vis) absorption spectrum was measured using Hitachi UV spectrometer U3010. PL spectra were obtained using Hitachi F-4500 fluorescence spectrophotometer at room temperature. The Fourier-transform infrared (FTIR) spectra were collected by a Bruker EQUINOX55 spectrometer equipped in absorbance mode.

The TiO₂/PS sample was firstly characterized by XRD and EDS, as shown in Fig. 1. The XRD pattern accords with the standard pattern of anatase TiO₂. As is known, the anatase phase is interesting in corrosive environments with its mechanical resistance and good stability^[12]. It is clear that the sample is composed of only four expected atoms (see the inset of Fig. 1), and the molar ratio of O:Si:Cl:Ti in the sample is 43.14:46.96:0.65:9.24. It is seen that a quantity of TiO₂ is deposited on the surface of PS and also there is still some Si remaining. Figure 2 shows the UV-vis absorption spectrum of TiO₂/PS. It can be seen that TiO₂/PS composite systems possess intense increase in absorption at about 3.2 eV and this

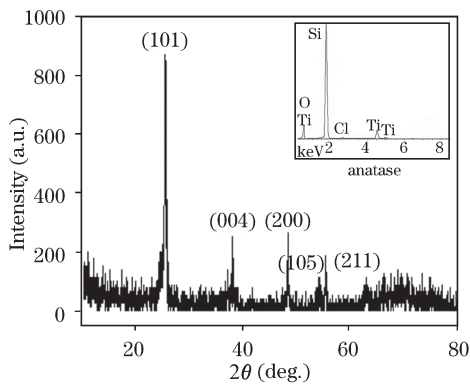


Fig. 1. XRD patterns and (inset) EDS spectra for the TiO_2/PS composite system.

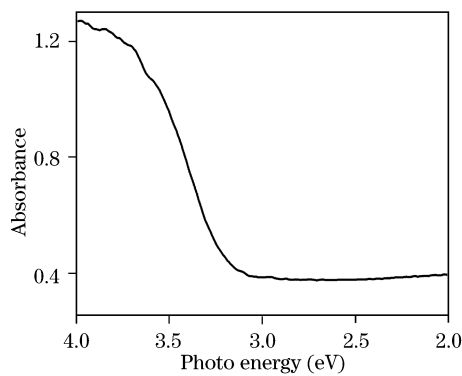


Fig. 2. UV-vis absorbance spectra of TiO_2/PS .

energy is well consistent with that of the crystalline bulk anatase (3.25 eV)^[10].

The room-temperature PL spectra of the TiO_2/PS composite system and PS with the excitation wavelength of 320 nm are presented in Fig. 3. The PL spectra of TiO_2/Si are also depicted in Fig. 3 for comparison. We can see a broad blue luminescence after the deposition of TiO_2 . A new PL peak is formed at around 400 nm both in TiO_2/PS and TiO_2/Si . Moreover, the blue intensity of the TiO_2/PS system is stronger than that of TiO_2/Si and PS. Additionally, PS has an emission peak at around 570 nm, which is more obvious and stronger under the excitation at 370 nm (not shown here). However, after the deposition of TiO_2 , this green-yellow emission degrades dramatically (Fig. 3) and the same phenomenon

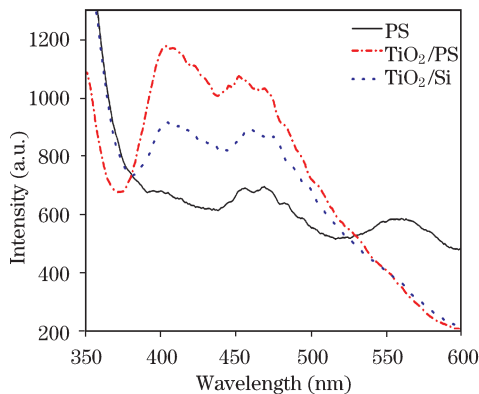


Fig. 3. Room temperature PL spectra of PS, TiO_2/Si , and TiO_2/PS with the excitation wavelength of 320 nm.

is also observed under the excitation at 370 nm.

The broad blue luminescence of the composite system seems to be caused by the interaction between PS and TiO_2 . Till now, the mechanism responsible for the origin of PS luminescence is still controversial, though several modes have been suggested. It was reported that high visible PL of PS could be attributed to the high porosity^[13], therefore, high porosity caused the green-yellow emission of PS we prepared. The SEM picture of PS shown in Fig. 4(a) supports this point, from which we can see the macropore which should be covered with luminescent mesoporous and microporous materials^[13]. Qin *et al.* have demonstrated the blue-light emission of PS due to the Si oxide layers surrounding the nanoscale Si units and the PL peak position of blue-light-emitting PS approximating to that of Si oxide^[14]. When TiO_2 is deposited on PS at 900 °C for 30 min, the blue-light emission intensity at around 470 nm increases, since the PS or Si substrate is oxidized and the quenching of green-yellow emission of PSi could be attributed to either the decrease of Si-H bond or the nonradiative recombination center formed by nanostructured TiO_2 . The FTIR spectra shown in Fig. 5 indicate a considerable decrease in the number of Si-H bonds and the broad band around 3400 cm^{-1} due to the Si-OH bonds^[15]. These support the above assumption and we suppose that it would improve the PL stability from the composite system after 900 °C oxidation, since Si-O bond is more stable in air.

On the other hand, the new PL peak of TiO_2/PS is formed at about 400 nm and the enhancement of blue-light emission intensity at around 470 nm is obtained, which are attributed to different microstructures of the sample surfaces (Fig. 4). It is seen from Fig. 4(b) that there are microspheres which would be

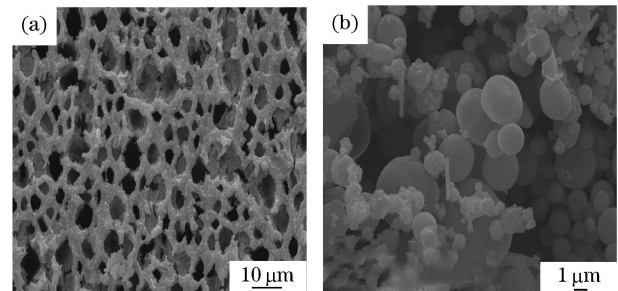


Fig. 4. SEM images of (a) PS and (b) TiO_2/PS .

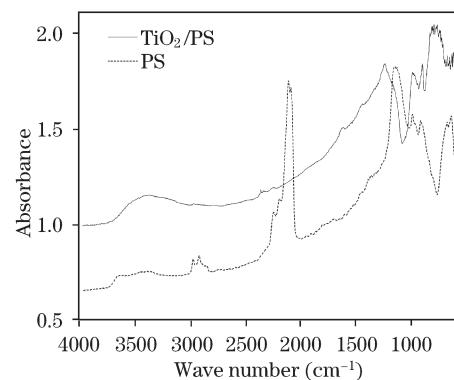


Fig. 5. FTIR spectra of PS and TiO_2/PS .

the polymers containing TiO₂ nanoparticles and also there are still some Si nanocrystals remaining on the surface of TiO₂/PS. According to the literature, it is difficult to observe PL phenomenon at room temperature for bulk TiO₂ even in monocrystal state^[16]. However, clear PL can be observed from nano-TiO₂^[10,17-19]. The blue emission from dispersible anatase TiO₂ nanocrystals corresponds to indirect transitions $\Gamma1b \rightarrow \Gamma2b$ (3.05 eV) and $\Gamma1b \rightarrow \Gamma2a$ (2.91 eV) due to oxygen vacancies^[10] and it could also be attributed to the good crystallinity of TiO₂ nanocrystals and quantum-size effect^[19]. In addition, there is no emission of TiO₂ nanocrystals without thermal treatment^[19]. Consequently, it can be concluded that the reason for the blue emission is not only PS or Si substrate being oxidized but also the TiO₂ nanocrystals and thermal treatment at 900 °C, and the blue intensity of the TiO₂/PS is stronger than that of TiO₂/Si because more TiO₂ is deposited on PS with a larger surface area.

In conclusion, a TiO₂/PS composite system has been successfully prepared by CVD. There are some TiO₂ microspheres observed by SEM and the TiO₂ films present orientation along the anatase phases. The PL spectrum of TiO₂/PS shows a broad blue luminescence and is stronger than that of TiO₂/Si, which proves that the TiO₂/PS composite system is significant for developing Si-based blue light emission optoelectronic devices. It is also important that these TiO₂ microspheres would be potential for advanced optoelectronic applications.

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