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Raman scattering in In/InO$_x$ core–shell structured nanoparticles*

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The properties of Raman phonons are very important due to the fact that they can availably reflect some important physical information. An abnormal Raman peak is observed at about 558 cm^{-1} in In film composed of In/InO$_x$ core–shell structured nanoparticles, and the phonon mode stays very stable when the temperature changes. Our results indicate that this Raman scattering is attributed to the existence of incomplete indium oxide in the oxide shell.

Keywords: Raman scattering, core–shell structure, indium, nanoparticles

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1. Introduction

Raman spectroscopy has been recognized as one of the most sensitive methods to study the structural properties of materials, especially for crystalline quality, structural changes, and disorder caused by doping, stress or dislocations.[1–3] Recently, core–shell structured nanoparticles have attracted intensive interest because of their unique optical, magnetic, and catalytic properties. Raman scattering studies of phonon modes are of fundamental importance to understand their structural and optical properties.[4,5] In previous studies, surface optical (SO) phonon mode, which is sensitive to the shell thickness, has been found in core/shell CdSe/ZnS quantum dots[6] and Zn/ZnO core–shell structured nanoparticles.[7] In the context of semiconductor nanowires, Raman spectroscopy has been used to study strains in GaAs/GaP,[8] GaAs/MnAs,[9] and Si/Si$_{1-x}$Ge$_x$[10] core–shell structures, as well as strains induced by bending.[11] In recent years, indium has attracted much attention because of its wide applications in electronic and optoelectronic devices, for example, indium tin oxide (ITO) and indium oxide (In_2O_3) can be considered as promising materials because of their conductive and optical properties. In this work we study in depth the structure, composition, crystalline phase, phonon modes, and disorder effects in In/InO$_x$ core–shell structured nanoparticles, by combining X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) with Raman measurements.

2. Experimental details

In/InO$_x$ core–shell structured nanoparticles were obtained by depositing indium grains on glass substrates (thickness of 0.17 mm) by radio-frequency (RF) magnetron sputtering (ULVAC ACS400-C4) with an RF power of 30 W and a working pressure of 0.57 Pa for 1000 s by one-off, two-layer, four-layer, eight-layer, twelve-layer deposition respectively, oxygen was introduced into the deposition chamber during the sputtering intervals. The thin films with incomplete indium oxide were deposited on glass substrates by introducing oxygen into the sputtering chamber through a controllable leak valve with the oxygen flux from 0.1 sccm to 0.5 sccm throughout the deposition.

Morphologies of the In/InO$_x$ core–shell structured nanoparticles were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800). The crystal structures of the In/InO$_x$ core–shell structured nanoparticles were analyzed by high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and X-ray diffraction (XRD, Philips X'pert Pro). Micro-Raman scattering spectra were acquired by a micro-Raman spectrometer (RenishawinVia Reflex).

3. Results and discussion

Figures 1(a)–1(e) shows the SEM micrographs of In/InO$_x$ core–shell structured nanoparticles sputtered different times

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from one to twelve. The oxidation shell surrounding the indium grain is formed by the oxygen-exposure process during the sputter interval. The more the deposition times, the smaller the grains are, due to the fact that the thin oxidation layer can interrupt the ripening process and restrict the nucleation growth. As is well known, In_2O_3 is the only stable one in all of indium oxides and the normal volume phonon vibration modes of perfect In_2O_3 crystal are at 130 cm^{-1}, 300 cm^{-1}, 360 cm^{-1}, 490 cm^{-1}, and 625 cm^{-1} respectively. For the core–shell In/InOx nanoparticles as shown in Fig. 1(f), however, we can see completely different Raman scattering spectra, which exhibit an abnormal and dominant Raman peak at about 558 cm^{-1} for all samples with different grain sizes, which is far from all the normal volume phonon vibration modes of perfect In_2O_3 crystal.

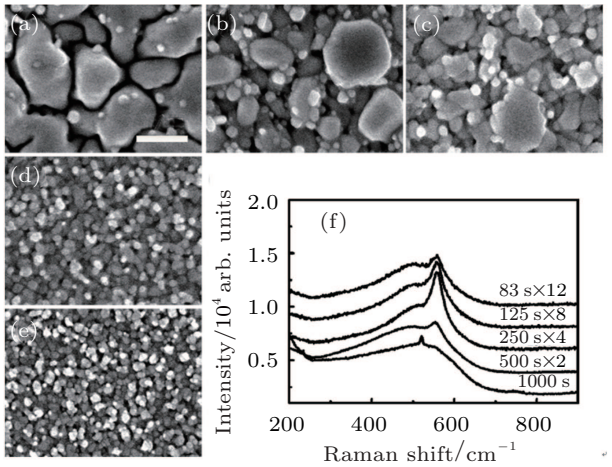


Fig. 1. SEM images, Raman spectra of In/InO_x core–shell structured nanoparticles deposited for different times, showing films deposited (a) one time (1000 s), (b) twice (500 s×2), (c) four times (250 s×4), (d) eight times (125 s×8), (e) twelve times (83 s×12) respectively, (oxygen was introduced into the deposition chamber during all the sputtering intervals), and (f) Raman spectra.

Figure 2 shows the Raman spectra of In/InO_x core–shell structured nanoparticles prepared by eight-time depositions under the different temperature conditions. As shown in the figure, locations of the abnormal phonon Raman peaks have the same shifts for the different temperatures, demonstrating that the abnormal phonon Raman peak is insensitive to the fabrication temperature. Such Raman spectra dominated by nonvolume mode, to the best of our knowledge, have not been reported so far in In/InO_x core–shell nanoparticles.

To further understand the origin of the abnormal Raman peak, XRD and TEM are used to study the compositions and crystal structures of the nanoparticles. The X-ray diffraction patterns of In/InO_x core–shell structured nanoparticles deposited for different times are shown in Fig. 3. The peaks can be assigned to (2 0 0), (2 2 0) planes of Si and (1 0 1), (0 0 2), (1 1 0), (1 1 2), (2 0 0) planes of In with body-centered structure respectively. The XRD spectra of In/InO_x core–shell structured nanoparticles deposited eight times are shown in the inset. The spectra can be fitted by two peaks at about 32.95° and 33.05°, which correspond to (2 0 0) plane of Si and (1 0 1) plane of In. The peak intensity decreases with increasing the deposition times, owing to the fact that the grain sizes of In/InO_x core–shell structured nanoparticles decrease, which is in good agreement with the SEM results. It can be confirmed from results of XRD that the nanoparticle contains indium crystals core and the thin oxidation layer as shell.

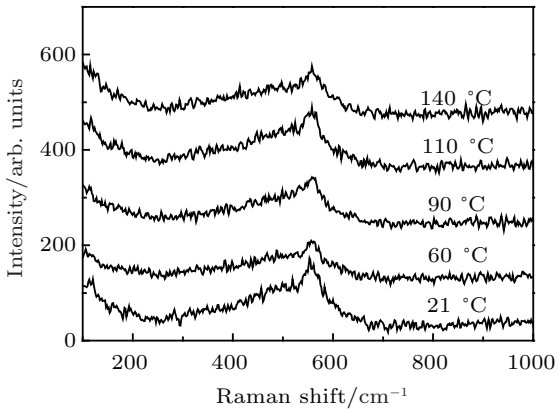


Fig. 2. Raman spectra of In/InO_x core–shell structured nanoparticles deposited eight times (125 s×8) at different temperatures.

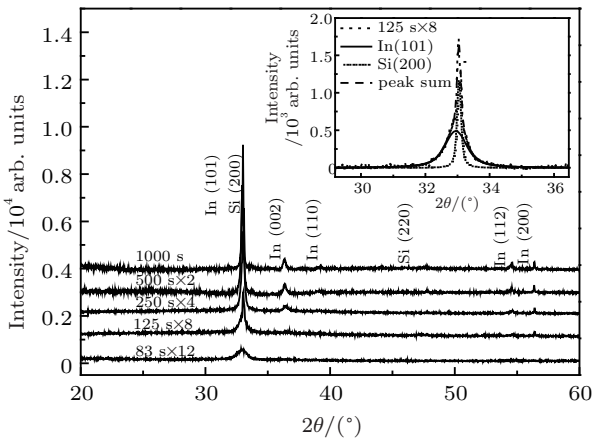


Fig. 3. XRD spectra of In/InO_x core–shell structured nanoparticles deposited different times. The inset shows the XRD spectra of In/InO_x core–shell structured nanoparticles deposited eight times.

Generally, for transmission electron microscopy (TEM), the thinner the film, the better the HRTEM image is. Here the thickness of In/InO_x core–shell structured nanoparticles deposited for 1000 s is about 90 nm, and it is too thick to obtain a good HRTEM image to distinguish the crystal indium core from amorphous indium oxide shell. Thus we choose a thinner sample (50 s×4) which is fabricated by the same multiple-depositing method. For electron energy loss spectroscopy (EELS), the nanoparticles deposited for 200 s (50 s×4) are too small to obtain the details because of only several nanometers resolution. Additionally, for 'multi-layer' In/InO_x core–shell

structured nanoparticles, it is hard to observe whether amorphous indium oxide shell is formed, hence nanoparticles deposited only once (200 s) are adopted here. Note that the thinner samples mentioned above have no influence on scientific essence of the characterization. The SAED pattern, HRTEM image, and EELS mapping of indium and oxygen elements of In/InO_x core–shell structured nanoparticles are shown in Figs. 4(a)–4(c). As can be seen in Fig. 4(b), the nanoparticle consists of a well-crystal core and amorphous surface. The body-centered cubic structure of indium core is further confirmed by SAED pattern, which is in agreement with the XRD result. The EELS mappings of indium and oxygen elements reveal the amorphous indium oxide shell. Indium has no Raman signal, so the new peak at 558 cm^{-1} may originate from the amorphous indium oxide shell. As is well known, in an infinite perfect crystal the phonons near the center of Brillouin zone (BZ) ($l = 0$) contribute to Raman scattering due to the momentum conservation law between phonons and incident light. However, for amorphous medium, the translational symmetry that characterizes crystals is lost, causing the correlation functions to be localized. Under natural conditions, the oxidation process of indium is uncertain and complicated. The product is amorphous and has a multi-component and complex chemical structure. The complex incomplete oxidation state may be the reason for the occurrence of new Raman peak of the In/InO_x core–shell structured nanoparticles.

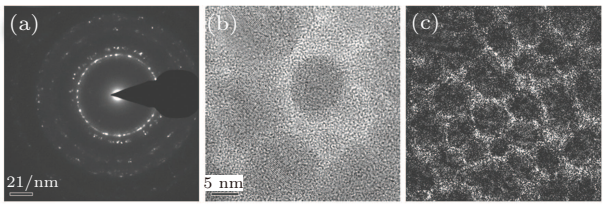


Fig. 4. In/InO_x core–shell structured nanoparticles deposited four times (50 s×4) , showing (a) SAED pattern, (b) HRTEM image; (c) EELS map of In/InO_x core–shell structured nanoparticles deposited one time (200 s), the indium and oxygen map (black is indium while white is oxygen).

Moreover, we obtain incomplete indium oxide films by introducing oxygen into the sputtering chamber with the fluxes ranging from 0.1 sccm to 0.3 sccm throughout the deposition of indium nanoparticles (see Figs. 5(a)–5(c)). The indium is incompletely oxidized and tended to form amorphous indium oxide (InO_x, x depends on the flux). As there is an extremely small amount of oxygen, the main composition of the thin film is still indium crystal of body-centered cubic structure (see Figs. 5(d)–5(f)). As the oxygen flux increases, the grain size decreases, owing to the fact that the oxygen can suppress the growth of big grains and promote the nucleation process to some extent. Thus we obtain the thin films which are composed of indium nanocrystals and amorphous InO_x. The Raman spectra are shown in Fig. 6, the intensity and position are apparently affected by oxygen flux. As oxygen flux increases, the intensity decreases and the band has a shift. The shift of the broad Raman peak position is closely related to the variation in the bond nature in the film. When the oxygen flux is 0.2 sccm, the Raman band is blue-shifted and broadened with a center at 558 cm^{-1}. As is well known, there exist amorphous InO_x and a great number of defects, such as grain boundaries, surfaces, and oxygen vacancy in the film. We believe that such a Raman peak results from the complex incomplete oxidation state.

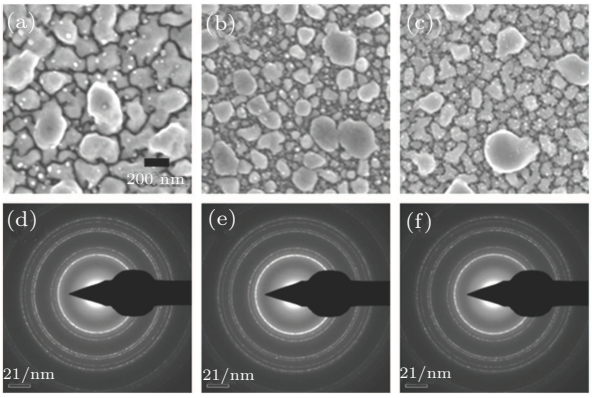


Fig. 5. SEM images and SAED patterns of incomplete indium oxide films deposited with the oxygen fluxes ranging from 0.1 sccm to 0.3 sccm.

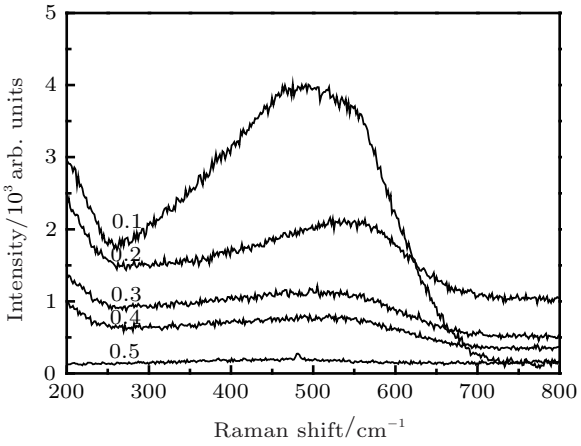


Fig. 6. Raman spectra of incomplete indium oxide thin films deposited with the oxygen fluxes ranging from 0.1 sccm to 0.5 sccm.

4. Conclusions

In this paper, we obtain In/InO_x nanoparticles with indium crystal core and amorphous indium oxide shell by magnetron-sputtering and natural oxidation. An abnormal phonon Raman peak at 558 cm^{-1} is observed in the In/InO_x core–shell structured nanoparticles, and it is insensitive to the fabrication temperature. Such a Raman scattering spectrum is attributed to the existence of amorphous incomplete indium oxides and a great number of defects in the amorphous shell.

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