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Evolution of Raman spectra in *n*-InAs wafer with annealing temperature

H.Y. Deng*, J.H. Guo, Y. Zhang, R. Cong, G.J. Hu, G.L. Yu, N. Dai*

National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, China

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ABSTRACT

The influence of annealing temperature on the optical properties of surface electron accumulation layers in *n*-type (1 0 0) InAs wafers has been investigated by Raman spectroscopy. It exhibits that Raman peaks due to scattering by unscreened LO phonons disappear with increasing temperature, which indicates that the electron accumulation layer in InAs surface is eliminated by annealing. The involved mechanism was analyzed by X-ray photoelectron spectroscopy, X-ray diffraction and high-resolution transmission electron microscopy. The results show that amorphous In_2O_3 and As_2O_3 phases are formed at InAs surface during annealing and, meanwhile, a thin crystalline As layer at the interface between the oxidized layer and the wafer is also generated which leads to a decrease in thickness of the surface electron accumulation layer since As adatoms introduce acceptor type surface states.

1. Introduction

It is interesting for scientists to investigate the generation mechanisms and optoelectronic properties of charge accumulation or depletion layers located in semiconductor surfaces, since it gives us an insight into their surface structures and electronic states which dramatically affect the electrical properties of semiconductor optoelectronic devices [1–4]. Generally, electron depletion layers are formed in *n*-type semiconductor surfaces such as GaAs, GaSb, and InP with their surface Fermi levels pinned within band gaps [5,6]. The surface of InAs, however, is distinctive and an electron accumulation layer has always been observed whether the wafer is *n* or *p*-type. Many research works have been made to clarify the involved generation mechanism [4,7–11]. Noguchi et al. [4] studied the electronic structures of clean InAs (1 0 0) surfaces by *in situ* high-resolution electron-energy-loss spectroscopy (HREELS) and found that surface electron accumulation layers were formed and changed reversibly with surface reconstructions. Both surface electron accumulation and depletion layers were observed by Piper et al. [9] and attributed to the ionized surface states caused by unoccupied anion-on-cation antisite defects and occupied cation-on-anion antisite defects, respectively. Recently, using the first-principle theory, Weber et al. [1] have systematically calculated the positions of surface states induced by dangling bonds, vacancies and adatoms of In and As and found that In adatoms were the only native defects that can induce a surface electron accumulation layer, since they could introduce singly occupied defect states above the conduction band minimum (CBM) which act as surface donors. These results show that the electron accumulation layer in InAs surface is caused by surface defects, which leads to the electron concentration in the surface being higher than in the underlying wafer. Hence surface treatments such as chemical modification [12] and metal atoms adsorption [13] have been used to adjust the thickness of the electron accumulation layer. These methods, however, are not only complicated but also difficult to accurately control the thickness. In this paper, we found that the properties of surface electron accumulation layers in *n*-type (1 0 0) InAs wafers could be easily controlled by rapid thermal annealing. The influence of annealing temperature on the thickness of accumulation layers was monitored by Raman spectrum. The involved evolution mechanism is clarified by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).

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* Corresponding authors. Tel.: +86 21 25051872; fax: +86 21 65830734.
E-mail addresses: hydeng@mail.sitp.ac.cn (H.Y. Deng), ndai@mail.sitp.ac.cn (N. Dai).

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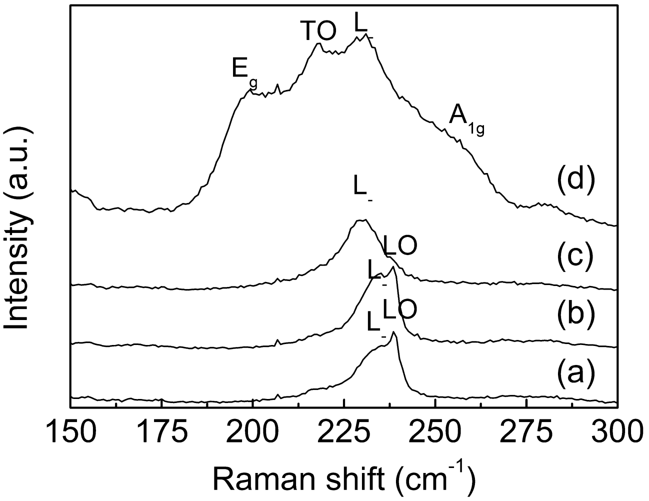

Fig. 1. Raman spectra of InAs wafers before (a) and after annealed at 400 °C (b), 450 °C (c) and 500 °C (d) for 5 min, respectively.

2. Experimental

The InAs used for heat treatment was *n*-type ($n \sim 10^{16}$ cm^{-3} at room temperature) one side well-polished undoped EPI-ready single crystal wafer with (1 0 0) direction and 450 ± 25 μm thickness, which was grown by liquid encapsulated Czochralski (LEC) method [14]. The InAs wafers were treated in a rapid thermal annealing furnace, respectively. The wafer was firstly placed on the sample tray in the chamber, and then the furnace was quickly raised to the annealing temperature (400, 450 or 500 °C) within 5 s and then held for 5 min. Once the furnace stopped heating, the wafer was immediately taken out and carefully placed into a glass beaker until it was completely cooled. Raman spectroscopy was used to monitor the change of surface electron accumulation layers utilizing scattering by the unscreened longitudinal optical (LO) phonons [15], which was carried out in the backscattering geometry by Tokyoinstru Nanofinder 30 spectroscopy with an 1800 lines/mm grating at room temperature. The wavelength of excitation light was 532 nm, and the laser power of 1 mw was used in order to avoid local heating effect. The XPS measurement was performed using Perkin Elmer RBD upgraded PHI-5000C ESCA system with Mg K_α radiation ($h\nu$ = 1253.6 eV) at about 5×10^{-8} Pa. Using Bruker D8 Discover diffractometer, the XRD spectra were measured by the Cu $K_{\alpha 1}$ line with the wavelength of 0.15406 nm. The cross-sectional HRTEM images were measured on the specimens prepared by Ar ion milling with liquid nitrogen cooling to keep wafers stable. The TEM measurement was operated at 200 kV.

3. Results and discussion

Although all InAs wafers were cut from the same ingot, four wafers that have almost the same Raman and XRD spectra were selected for annealing experiments in order to eliminate the slight difference between these wafers. Fig. 1 shows the Raman spectra of InAs wafers before and after rapid thermal annealing at 400, 450 and 500 °C for 5 min, respectively. By comparing cures (a) and (b) it can be seen that the annealed wafers have almost the same Raman scattering curves as the unannealed wafers when the annealing temperatures are below 400 °C, in which two Raman scattering peaks appear. The peak at 234 cm^{-1} is attributed to the low-frequency branch (L_-) of coupled LO-phonon-plasmon modes. The peak at 239 cm^{-1} is assigned to unscreened scattering from LO phonons in the surface electron accumulation layers. Buchner and Burstein [15] have explained the physical origin of occurrence of LO mode in heavily doped *n*-type InAs single wafers using the large-wave vector (large-*q*) scattering mechanism. They thought that the unscreened LO mode was derived from the accumulation layer in InAs surface and caused by decoupling of L_- mode when the wave vector of L_- mode was larger than the Fermi–Thomas screening wave vector q_{FT} so that carriers could not screen macroscopic field [16]. Hence Raman spectroscopy could be effectively used to probe the evolution of surface charge accumulation layers. When the annealing temperature increases to 450 °C, however, two interesting features are found in curve (c). One is that the L_- mode shifts toward the low frequency, indicating that the carrier concentration in InAs wafer increases with increasing the annealing temperature from 400 to 450 °C according to Buchner and Burstein's result [15]. The similar conclusion that heat treatment at temperatures of 450 °C increases the carrier concentration of *n*-type InAs has also been drawn by Dixon and Enright [17] using Hall measurement. The other obvious feature is that the LO phonon peak disappears. According to previous results [12,18], the thickness of the surface electron accumulation layer can be determined from Raman spectrum by the following equation:

$$\frac{I_{LO}}{I_{L_-}} = \frac{R_{LO}}{R_{L_-}}(e^{2\alpha d} - 1), \quad (1)$$

where I_{LO} and I_{L_-} are the Raman scattering intensities of LO and L_- modes, R_{LO} and R_{L_-} are the scattering coefficients respectively, α is the absorption coefficient of InAs at 532 nm, and d is the thickness of the electron accumulation layer. Hence it can be inferred from Eq. (1) that the disappearance of LO mode means that the thickness of the surface electron accumulation layer decreases to zero and the accumulation layer is eliminated. When the annealing temperature increases to 500 °C, besides L_- peak three additional scattering peaks appear (see curve (d)). The peak at 218 cm^{-1} corresponds to the transverse optical (TO) phonon mode caused by the presence of disorder [19,20], which should not be observed since TO modes in (1 0 0)-oriented InAs wafer is forbidden in the backscattering configure. Two weak peaks at about 195 cm^{-1} and 257 cm^{-1} are assigned to the E_g and A_{1g} modes from crystalline (*c*-) As [21,22]. Compared with curve (c), the position of L_- peak does not shift, indicating that the carrier concentration in InAs wafer has little change with increasing the annealing temperature to 500 °C. It is also noted that LO mode is still absent at this annealing temperature.

In order to clarify the evolution mechanism of surface electron accumulation layers, we firstly performed XPS measurements on these sample surfaces, which are shown in Fig. 2. Besides As 3*d*, In 3*d* and O 1*s* peaks, C 1*s* peaks is also observed. The existence of C 1*s* peak is due to surface contamination when the samples were exposed to atmosphere. According to the position of the C 1*s* peak at the binding energy of 284.6 eV, we calibrate the overall XPS spectra. To clearly show the fine structures of the spectra, Fig. 2 presents only the calibrated high resolution spectra of As 3*d*, In 3*d* and O 1*s* peaks with the characteristic of Gaussian function. Curve (a) gives the XPS spectrum of the unannealed InAs wafer. The peak at 40.4 eV corresponds to the binding energy of As $3d_{5/2}$ in InAs and near this peak a weak peak at 44 eV appears which could be assigned to the As $3d_{5/2}$ level emission in As_2O_3 since its O 1*s* peak at 531.5 eV is also observed. The peak at 444.4 eV is consistent with the binding energy of In $3d_{5/2}$ in InAs. Hence InAs surface is slightly oxidized to form As_2O_3 at room temperature. When the wafer was annealed at 400 °C for 5 min (see curve (b)), the intensity ratio of As $3d_{5/2}$ peaks between InAs and As_2O_3 decreases, indicating that the amount of As_2O_3 at InAs surface increases. The O 1*s* peak at 530.9 eV is attributed to the binding energy in In_2O_3, and correspondingly the peak at 444.5 eV is mainly contributed by the In $3d_{5/2}$ emission in In_2O_3. Although InAs and As_2O_3 do exist at the surface, the peaks of In $3d_{5/2}$ in InAs and O 1*s* in As_2O_3 could not be decomposed from curve (b) by Lorentzian–Gaussian optimization since they have a