Periodic Nanostructures and Optical Properties of InP Induced by Femtosecond Laser Pulses

Shanshan Tian¹, Zhipeng Wei¹, Haifeng Zhao², Xian Gao¹, Xuan Fang¹, Jilong Tang¹, and Xiaohui Ma¹

¹ Changchun University of Science and Technology, Changchun 130022, China
² Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun, 130033, China

In this letter, InP periodic nanostructures were synthesized by linearly polarised femtosecond laser. Perfect morphologies of InP nanostructures can be obtained under an appropriate laser power. Further, to restrain surface states of InP, the Al₂O₃ layers were deposited on InP nanostructures by atomic layer deposition (ALD). The optical properties of InP nanostructures were investigated by Raman and Photoluminescence (PL). And the transverse optical (TO) peak and novel luminescence emission can be observed due to the formation of the periodic nanostructures.

Keywords: InP Periodic Nanostructures, Atomic Layer Deposition, Photoluminescence, Raman Spectrum.

1. INTRODUCTION

With high carrier mobility and proper band energy, InP has been considered as the important semiconductor, which has many applications in the field of optoelectronics. In addition, with the novel optical and electric properties, low dimension materials have been studied extensively. Nowadays, nanotechnology and the related technologies are playing an important role in technological development and research.¹ Nanoporous materials and nanofilms have potential applications in many fields, such as physicochemical field,²,³ biomedical field.² The engineered nanoparticles made from noble metals, rare-earth oxides or semiconductors are becoming the centers of the future nanotech developments.⁵

The generation of periodic nanostructure upon femtosecond laser is a very universal phenomenon. Since such periodic structures on semiconductor by laser-irradiated was first observed by Birnbaum in 1965,⁶ a lot of studies have been researched on metals,⁶,⁷ semiconductors³⁴⁴ and dielectrics.⁵ Since the energy density threshold value of the femtosecond laser ablation can be controlled precisely, and the range of thermal diffusion is small, femtosecond laser ablation becomes an effective tool for micro-process of sub-micron range, and has been expected to be applied in grating, optical waveguides, batteries and other micro- and optoelectronic devices.⁷ Surface states exact on semiconductor surface.¹⁸ These states could generate nonradiative recombination centers or large leakage currents, which could affect performance of the devices. Thus, for III-V materials, passivation treatment is essential. Among them, (NH₄)₂S solution passivation method is a effective method,¹⁹⁻²³ which can easily remove the oxide layers on the surface. Meanwhile, the formed S layers could prevent surface atoms oxide again. However, thickness of the S layers need to be controll accurately.²⁴

With the advantages of simplicity, reproducibility, atom layer deposition (ALD) is a unique technique for the deposition of thin layers on many substrates.²⁵ In Zhernoklev's report, HfO₂ were deposited on S passivated GaSb, by controlling the thickness of HfO₂ layers. Surface states can be depressed effectively. In addition, Aluminum oxide (Al₂O₃) films can also be used as the passivation layers.²⁶ Huang deposited Al₂O₃ on In₁₅ Ga₈₅ As/GaAs heterostructures, then obtained Al₂O₃/InGaAs/GaAs heterostructures with low electrical leakage current density and low interfacial density of states.²⁷

In this paper, InP nanostructures and Al₂O₃ coated InP nanostructures were obtained using femtosecond laser and ALD. The morphologies were characterized by scanning
Periodic Nanostructures and Optical Properties of InP Induced by Femtosecond Laser Pulses

Tian et al.

2. EXPERIMENTAL DETAILS

In this paper, the 500 μm thickness n-type InP wafer was irradiated in vacuum using linearly polarized femtosecond laser with wavelength of 800 nm, pulse duration of 50 fs. The power of laser is from 60 mW. The laser beam should always be directed perpendicular to the surface of samples, the sweeping velocity is 3 mm/s.

Al₂O₃ layers were deposited using LabNano™9100 ALD system from Ensure Nanotech (Beijing). For Al₂O₃ growth, trimethylaluminium (TMA) and water were used as precursor source and high purity nitrogen (N₂) was used as the purging gas. The pulse time of water and TMA was 20 ms and the purging time was 5 s. The growth temperature was 250 °C. The cycles of growth were 100, 150 and 200 for Al₂O₃.

The ablation morphology was characterized by means of a scanning electron microscope (S-4200). Micro Raman spectroscopy was used to obtain information concerning the crystalline structure of the ablated area. Raman spectra were recorded in 180°-backscatter geometry on samples oriented perpendicularly to the excitation beam direction (z) with liquid nitrogen cooled CCD-multichannel detector. The surfaces were excited by Ar⁺ laser with the 632 nm emission line. The PL spectra were measured using Nanometrics RPM2000 photoluminescence spectrometer. The frequency doubled Nd:YAG laser (532 nm) with 100 mW is used as the excitation source.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the periodic nanostructures on femtosecond laser irradiated InP wafer. The ripples are parallel to the laser polarization direction and it is contrast to the results of Bonse et al.⁹ and Borowiec et al.¹³ It is the same as the observation of Qian et al.²⁸ The width of ripples is about 460 nm and didn't coincide with the laser radiation wavelength. This result also contrast to the observation by Bonse et al.⁹ The deposition of Al₂O₃ films by ALD didn't change the periodic nanostructures, as we can see in Figure 1(b). The width of ripples didn't change either. The morphology of surface periodic nanostructures could be observed clearly through the Al₂O₃ films. It indicated that Al₂O₃ films are homogeneously deposited and have a high transparency.

Figure 2 shows the normalized room-temperature PL spectra of InP wafer (a) and InP nanostructures (b). For InP wafer, the emission peak located at about 1.37 eV came from the band-edge (BE) transition of InP.²⁴ For InP nanostructures, besides the BE emission, a novel broad emission band ranges from 1.6 eV to 2.15 eV could be observed in the PL spectra. Here, we deduced the emission is associated with a large size distribution of InP nanostructures.²⁵ From the SEM images, irradiated by femtosecond laser with wavelength of 800 nm, pulse duration of 50 fs and laser energy of 60 mW ranges from 1.48 eV to 2.18 eV. An obvious broad PL band ranges from 1.6 eV to 2.15 eV could be observed in the spectra of InP surface irradiated by femtosecond laser. This PL band is associated with a large size distribution of InP nanostructures.²⁵ We can observe that the sizes of the nanostructures aren't all the same in Figure 2. There are some small nanostructures distributed on the InP surface and many small size particles distribute on the nanostructures. The broad PL band shows an asymmetry on...
the intensity. It is caused by the wide distribution of InP nanostructures and the presence of complex surface states introduced by surface modification. The band-edge (BE) transition PL peaks located about 1.372 eV. In addition, the as-irradiated and uncoated nanostructures would promote the surface recombinations. The complex detects could quench the PL from surface nanostructures.

Figure 3 shows the room temperature (RT) PL spectra of the InP nanomaterials samples without and with Al$_2$O$_3$ films deposition for 100, 150, 200 cycles, respectively. All PL peaks have the almost same position at 1.37 eV, which is due to band edge (BE) emission. The BE peak positions did not vary with the thickness of Al$_2$O$_3$ shell layers coating. It can be clearly observed that the PL intensity strongly depend on the cycles of Al$_2$O$_3$ films. At first, the PL intensity increased with the cycle number of Al$_2$O$_3$ films, and reached a maximum intensity when the number of the cycles is 150. The PL intensity increases by a factor of 7.1 after depositing 150 cycles Al$_2$O$_3$ films. The origin of the enhanced BE emission of nanostructure InP can be explained by the following model. There are many dangling bonds on InP surface. During the irradiation process of femtosecond laser, three changing regimes could happen on the InP surface: melting, ablation and recrystallization. The dangling bonds would reappear during the three changing process. For the uncoated InP, oxygen and other impurities molecules are adsorbed by the surface nanostructure. These molecules trap the free electrons from the conduction band and become the charged molecules. These dangling bonds and the impurities molecules generate the surface states. Surface passivation of InP could reduce surface states density and increase photoluminescence intensity. The deposited layers bonded the surface dangling bonds and removed the adsorbed impurity molecules on the surface which leads to the reduction of nonradiative recombination centers. When the cycles of Al$_2$O$_3$ films increased to 200, the PL intensity decreased drastically. It is likely because the thick Al$_2$O$_3$ films prevent the emergent of the photoluminescence and can scatter light which results in weaker PL intensity.

Room-temperature Raman spectra are presented in Figure 4, which shows the spectra between 150 and 450 cm$^{-1}$. (a) Raman spectrum of bulk n-type InP (100) wafer, (b) nanostructure InP surface irradiated with the laser power of 60 mW, (c) nanostructure InP surface with 100 cycles Al$_2$O$_3$ films. The longitudinal optical (LO) phonon-peak appears at about 344 cm$^{-1}$ in spectrum (a). In the chosen excitation geometry, the transverse optical (TO) peak is forbidden by the Raman selection rules in InP (100). The TO phonon peaks are apparent in the spectra of the samples irradiated with femtosecond laser which appears at approximately 304 cm$^{-1}$. The phonon peak at 314 cm$^{-1}$ can be assigned as the L$_2$O-phonon Plasmon coupled (LOPC) mode in InP. Such coupled modes had been reported attribute to the doping concentration. The LO phonon peaks located at about 344 cm$^{-1}$ in the spectra of femtosecond laser irradiated samples and it is the same as the untreated InP bulk materials. The linewidth of the LO phonon peaks broadens and become asymmetrical towards the low frequency side, which is attribute to the coherence length of the phonons in the disordered material. The new broad band range from 360 cm$^{-1}$ to 450 cm$^{-1}$ is attributed to the phosphorus—phosphorous band vibration (P—P). Spectrum (b) and (c) are similar to each other. The Raman spectra indicate the crystalline structure of the material near the surface. From the identical intensity of the spectra lines, we can conclude that the InP crystalline is in a polycrystalline state (the molten InP resolidified in polycrystalline). So we can conclude that the crystalline state changes after irradiation by femtosecond laser and the InP crystalline is in a polycrystalline state.

4. CONCLUSIONS

In summary, sulphur-doped n-type InP wafer was irradiated in vacuum using linearly polarised femtosecond laser with wavelength of 800 nm, pulse duration of 50 fs and laser energy of 60 mW. The periodic nanostructures presented on the InP surface after the irradiation with
Acknowledgment: This work is supported by the National Natural Science Foundation of China (61006065, 61076039, 61204065, 61205193), National Key Lab of High Power Semiconductor Lasers Foundation (No. 9140C310101120C031115), Research Fund for the Doctoral Program of Higher Education of China (21022216110002, 20122161100001, 20122161200005), the Natural Science Foundation of Jilin Province (20101546), the Developing Project of Science and Technology of Jilin Province (20090139, 20090555, 20121816, 20120111), the Foundation of Department of Education of Jilin Province (20090150, 20101546), the Developing Project of Science and Technology of Jilin Province (2011JYT05, 2011JYT10, 2011JYT11) Changchun International Science and technology cooperation project (2010CC02), 2011M500861. Thanks for the help of D. D. Wang, Y. S. Yan, for the SEM measurement.

References and Notes