Unusual optical properties of type-II InAs/$GaAs_{0.7}Sb_{0.3}$ quantum dots by photoluminescence studies

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The optical properties of type-II InAs/$GaAs_{0.7}Sb_{0.3}$ quantum dots (QDs) were investigated by photoluminescence (PL). It is found that the peak position of PL spectra exhibits a significant blueshift under a moderate excitation level. The observed blueshift can be well explained by the band bending effect due to the spatially separated photoexcited carriers in a type-II band alignment. We also found that the PL spectra exhibit a strong in-plane polarization with a polarization degree up to 24%. The observed optical anisotropy is attributed to the inherent property of the orientation of chemical bonds at InAs/$GaAs_{0.7}Sb_{0.3}$ heterointerfaces.

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InAs-based quantum dots (QDs) provide potential applications in long wavelength optical-fiber communications. To obtain the required wavelength of 1.3 μm and 1.5 μm in QDs lasers, several methods have been used to reduce the influence of compressive strain effect, such as the strain reducing layer (SRLs), stacking QDs, and surface QDs.[1–3] Alternatively, type-II band alignment also provides an excellent way to lengthen emission wavelength.[4–7] For InAs QDs embedded in GaAsSb layers, it has been reported that the type-I/type-II transition occurs at an Sb composition of 14%.[4,5] In addition to the application in QDs laser, the type-II InAs/GaAsSb QDs heterostructures are potentially useful materials for photovoltaic devices due to their nature of the separation of photoexcited electrons and holes.[4–7] InAs/GaAsSb QDs system are therefore very attractive for both of academic interest and industrial application. However, the published reports on optical properties of this material system are still rather limited. Here, we present a detailed investigation of type-II InAs/$GaAs_{0.7}Sb_{0.3}$ QDs by photoluminescence (PL) measurement. It is found that a significant blueshift of the peak energy occurs under a moderate excitation power, which can be well explained by the band bending effect due to the spatially separated photoexcited carriers in type-II band alignment. In addition, a strong optical anisotropy is also found, which is attributed to the asymmetry of interface chemical bonds. In view of the mature growth process, InAs/GaAsSb QDs should be able to serve as a model system for the search of novel properties in type-II quantum structures.

The sample was grown in Stranski-Krastanov (SK) growth mode on an undoped semi-insulating GaAs (100) substrate by a VG V-80MKII solid-source molecular beam epitaxy machine.[8] After a 500 nm thick undoped GaAs buffer layer, the sample consists of a 2.0 ML InAs QDs embedded between $GaAs_{0.7}Sb_{0.3}$ layers grown at 485 °C, then a 60 nm undoped GaAs without growth interrupt, and a 500 nm undoped GaAs was grown at 500 °C. The antimony composition in the $GaAs_{0.7}Sb_{0.3}$ layer was determined using double crystal x-ray diffraction (DXRD) measurement. In addition, a sample containing a single layer of InAs/GaAs QDs (2.0 ML) was used for comparison.

For the structural measurement, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) studies were performed using a Philips Tecnai-F20 instrument. The scanning electron microscopy (SEM) images were recorded by a JEOL-JSM 6500 system. The PL spectra were measured by a Spectra Pro 300i monochromator and an InGaAs detector. An Ar-ion laser working at 514.5 nm was used as the excitation source. For the measurement of the polarization dependence of the PL spectra, a depolarizing filter was placed in front of the spectrometer to exclude the possible polarized character of the grating.

Figures 1(a) and 1(b) show the SEM images of the uncapped InAs QDs deposited on GaAs and $GaAs_{0.7}Sb_{0.3}$ layers, respectively. The size of the uncapped InAs QDs formed on GaAs is smaller than those on $GaAs_{0.7}Sb_{0.3}$, which is caused by the different surface strain field as reported previously.[9,10] Figure 1(c) clearly shows the [100]-axial cross-sectional TEM image of the InAs QDs embedded between $GaAs_{0.7}Sb_{0.3}$ layers with a total thickness of about 11 nm as marked by the separation of the two dash lines. But the actual shape of the InAs QD is unclear since the strain field may extend beyond the island boundary. We thus have performed the STEM measurement, which is known not to be influenced by the strain field. From the STEM image, the InAs QD is determined to be about 3.5 nm high and reveals a flat top as shown in Fig. 1(d). The combination of TEM and STEM images therefore clearly shows that the InAs QD

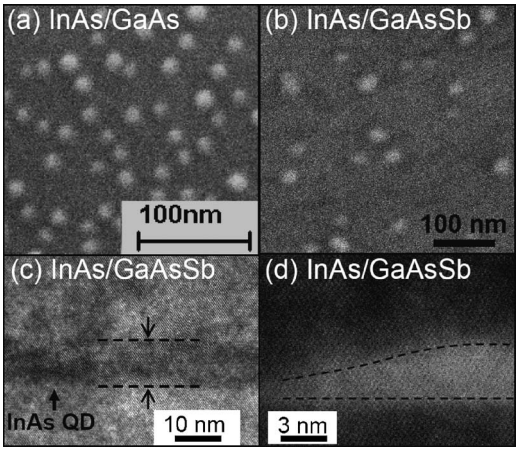

FIG. 1. Scanning electronic microscopy images of uncapped (a) InAs/GaAs and (b) InAs/$GaAs_{0.7}Sb_{0.3}$ quantum dots. (c) Transmission electron microscopy and (d) scanning transmission electron microscopy images of the InAs quantum dots embedded between $GaAs_{0.7}Sb_{0.3}$ layers.

is indeed sandwiched by GaAsSb layers. Each GaAsSb layer has a thickness of about 5.5 nm.

Figure 2 shows the PL spectra of InAs/GaAs and InAs/$GaAs_{0.7}Sb_{0.3}$ QDs under different excitation power at 20 K. The peak energy of InAs/$GaAs_{0.7}Sb_{0.3}$ QDs is smaller than that of InAs/GaAs QDs at the same excitation power. Quite interestingly, in spite of having a type-II band alignment, the InAs/$GaAs_{0.7}Sb_{0.3}$ QDs exhibit a strong emission with intensity close to that of the InAs/GaAs QDs at the same excitation condition. Besides, the linewidth of the emission spectra of the InAs/$GaAs_{0.7}Sb_{0.3}$ QDs is about 50 meV which is smaller than that of the analogous system of InGaAs QDs embedded between GaAsSb layers as reported previously.[6] Both of the bright emission and narrow linewidth indicate that the sample has an excellent quality. As shown in Fig. 3, in contrast to the unchanged peak energy of type-I InAs/GaAs QDs, we observe a giant blueshift of about 29 meV in InAs/$GaAs_{0.7}Sb_{0.3}$ QDs under a moderate excitation power. The value of the blueshift of the

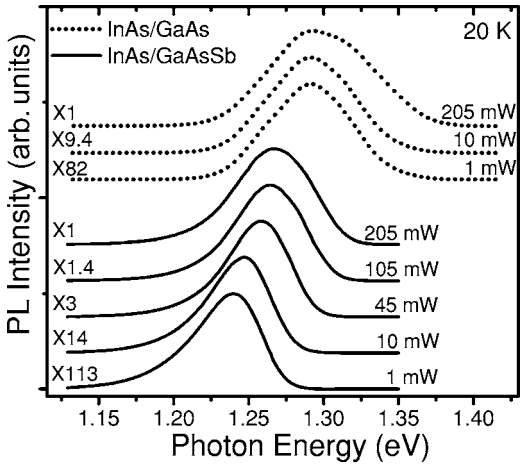

FIG. 2. Excitation power dependence of the photoluminescence spectra.

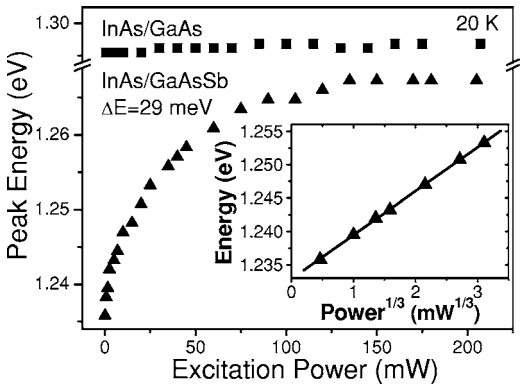

FIG. 3. Peak energy of photoluminescence spectra for InAs/GaAs (■) and InAs/$GaAs_{0.7}Sb_{0.3}$ (▲) recorded with different excitation level. The inset shows the peak energy of InAs/$GaAs_{0.7}Sb_{0.3}$ (▲) on the cubic root of excitation power (solid line).

InAs/GaAsSb QDs is close to 34 meV of the analogous structure in a previous report.[5] This peculiar behavior cannot be due to laser heating because it will cause a redshift in the band gap. The blueshift is too large to be caused by the state filling of the localized states due to interface roughness or alloy potential fluctuations.[11] We believe that the underlying mechanism of our observation is an intrinsic nature of the type-II band alignment of InAs/$GaAs_{0.7}Sb_{0.3}$. Figure 4 shows the schematic type-II band diagram for InAs/$GaAs_{0.7}Sb_{0.3}$ system with the band bending effect due to charge carriers transfer. The electrons and holes are confined in the InAs QDs and $GaAs_{0.7}Sb_{0.3}$ layer, respectively.[4,5]

The giant blueshift under a moderate optical excitation level can now be readily understood.[12] Qualitatively, it can be explained as follows. The spatially separated electrons and holes lead to the appearance of a strong electric field at the interface which in turn gives rise to the bending of the valence and conduction band. With increasing excitation power, the band bending effect becomes more pronounced,

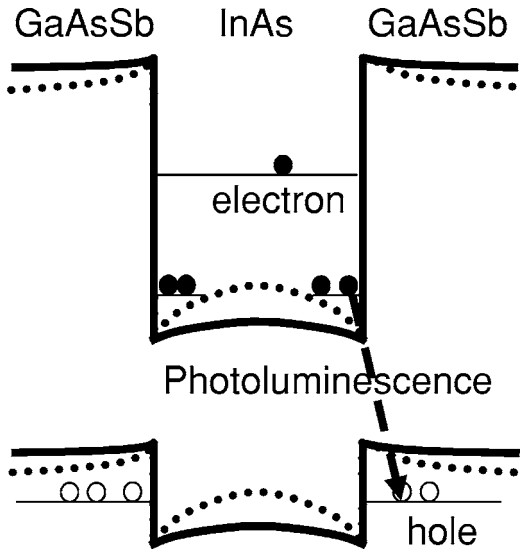

FIG. 4. Band-bending effect of the type-II band structure under low (solid line) and high (dash line) excitation power density.

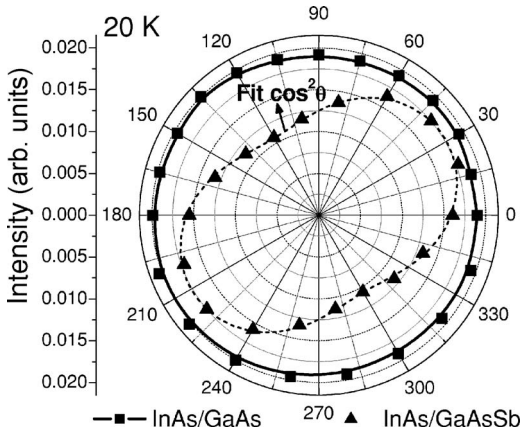

FIG. 5. Polar plot of the polarized photoluminescence intensity as a function of the polarizer angle for InAs/GaAs (■) and $InAs/GaAs_{0.7}Sb_{0.3}$ (▲) quantum dots. The dash curve is a $\cos^2\theta$ fit.

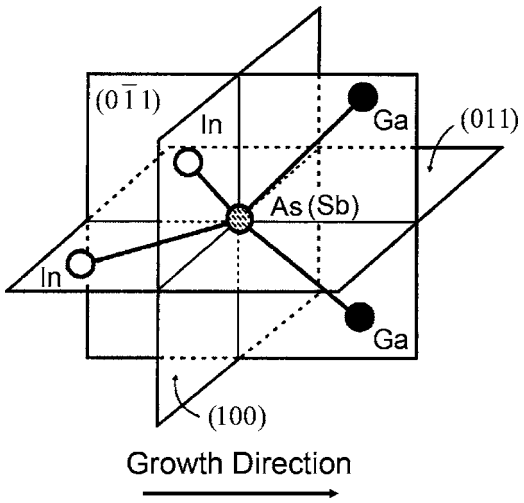

FIG. 6. Schematic diagram of the bond sequence of $InAs/GaAs_{0.7}Sb_{0.3}$ quantum dots.

and the accumulated electrons and holes will be confined in a narrower region near the interface. Consequently, the electron quantization energy is enhanced and the blueshift occurs. As the excitation power exceeds about 100 mW, the blueshift saturates due to the filling effect of energy states.

In order to analyze the blueshift quantitatively as shown in Fig. 3, we consider the change of the nonequilibrium carrier density due to photoexcitation. The strong localized carriers near the interface form a charged plane, and correspondingly, produce an approximated triangular potential well with an electric field of $\varepsilon \propto I^{1/2}$, where I is the excitation photon flux. The ground electron state E_c in a triangular well is given by[8,12]

$$E_c = \text{const} \cdot \varepsilon^{2/3} = \text{const}' \cdot I^{1/3}. \quad (1)$$

The electron quantization energy is thus expected to increase proportionally with the third root of the excitation power. As shown in the inset of Fig. 3, the PL peak energy can be described quite well by the third root of the excitation power obtained from Eq. (1). It indicates that the giant blueshift is indeed a peculiar property of the type-II heterostructure.

Besides, with increasing the excitation power, the line shape of type-I InAs/GaAs QDs remains unchanged as shown in Fig. 2. In contrast, the evidently asymmetric spectra of $InAs/GaAs_{0.7}Sb_{0.3}$ at low excitation power gradually turns into a symmetric shape. This behavior may be attributed to the fact that the built-in electric field due to surface charges can tilt the band edge, which will give rise to a nonuniform distribution of the photoexcited carriers in conduction and valence bands. Therefore, the line shape becomes asymmetric and results in the so-called quantum confinement Stark effect (QCSE).[13,14] With increasing excitation power, the internal electric field is screened by the photoexcited carriers, and therefore the linewidth gradually turns into a symmetric shape.

Additionally, we have performed the polarization dependence of PL spectra for InAs/GaAs and $InAs/GaAs_{0.7}Sb_{0.3}$ QDs, as shown in Fig. 5. In bulk semiconductors, the study of polarization dependent PL spectra is an efficient tool for obtaining the information about symmetry of structures and emission states. In semiconductor QDs, the bulk valance band is split into heavy-hole, light-hole, and spin-orbit band via quantum confinement and uniaxial strain.[15,16] These three bands have different polarization properties, in general, the lowest optical transition are related to geometric symmetries of the QDs. Indeed, for the type-I InAs/GaAs QDs, the isotropic emission light is consistent with the isotropic shape of uncapped QDs, as shown in Fig. 1(a). Quite surprisingly, the $InAs/GaAs_{0.7}Sb_{0.3}$ QDs exhibit a strong optical anisotropy as shown in Fig. 5. The polarization degree defined as $P \equiv (I_{max}-I_{min})/(I_{max}+I_{min})$ is as large as 24%, where the I_{max} and I_{min} are the maximum and minimum polarized emission intensities, respectively. From the SEM image as shown in Fig. 1(b), the uncapped InAs QDs grown on $GaAs_{0.7}Sb_{0.3}$ layer do not reveal an evidently anisotropic shape. Therefore, the observed optical anisotropy cannot be due to the geometric effect of the QDs. Besides, this behavior also cannot be attributed to a slight misorientation of the substrate which may give rise to a preferential orientation of steps at the interface. It is because both samples in our studies are grown on the same kind of substrate, and the InAs/GaAs QDs do not show any indication of anisotropic behavior.

We believe that the behavior arises from the type-II transition for electrons confined in the InAs QDs and holes confined in the $GaAs_{0.7}Sb_{0.3}$ layer, in which the recombination is due to the electron-hole wave function overlap across the interface within an extremely narrow region. Therefore, the transition oscillator strength is strongly correlated with the anisotropic property of interface chemical bonds.[17–19] Compared with the interior volume of a bulk material, a lower symmetry does exist in an isolated interface between two semiconductors. The resultant optical anisotropy has been observed previously in many semiconductor heterostructures with an AB/ABC-type combination.[18,19] More specifically, the in-plane anisotropy arises from the uncompensated polarization of chemical bonds across the interface, not found inside the bulk. A schematic diagram of the polarized chemical bonds for a GaAsSb layer capped on a InAs QD is shown in Fig. 6. In the zinc-blende structure, the interface of the

InAs/GaAsSb heterostructure consists of In-Sb, In-As, and As-Ga bonds. We can clearly see that the chemical bonds are strongly anisotropic, which is quite different from the bulk case. Therefore, the in-plane anisotropic characteristic inherently exists in the $InAs/GaAs_{0.7}Sb_{0.3}$ QDs studied here. To verify the anisotropic effect, we have rotated $InAs/GaAs_{0.7}Sb_{0.3}$ QDs sample by 90°, and found that the direction of the polarized emission also rotates by 90°. This result provides a further evidence to support the fact that the optical anisotropy does depend on the orientation of interface chemical bonds.

In order to clarify that the observed polarized PL spectra are induced by the anisotropic nature of the interface chemical bonds, we have performed the excitation power and temperature dependences of the polarization. It is found that the degree of polarization is insensitive to the change of excitation power in the range from 10 to 200 mW. The degree of polarization is also very stable with respect to the change of temperature from 10 to 200 K. These results can be used to rule out extrinsic mechanisms related to the in-plane anisotropy. For example, the built-in electric fields caused by unintentional doping will be screened under light irradiation. We can also exclude a significant role of localized states and nonradiative channels in the formation of the in-plane anisotropy. Since they will be gradually saturated by the excitation source and the thermally activated carriers will redistribute among them, which will change the transitions of carriers. We thus conclude that the polarization of the spatially indirect PL in $InAs/GaAs_{0.7}Sb_{0.3}$ is an inherent nature of the interface chemical bonds. Polarized PL measurements therefore provide a simple tool to probe interface anisotropy in semiconductor heterostructures.

In summary, the optical properties of type-II $InAs/GaAs_{0.7}Sb_{0.3}$ QDs have been investigated by PL measurements. In contrast to the InAs/GaAs QDs, it is found that the PL spectra show a giant blueshift under a moderate optical excitation level. This behavior can be interpreted in terms of the band bending effect due to the spatially photoexcited carriers in a type-II band alignment. We also found that the PL spectra exhibit a large in-plane polarization with the polarization degree up to 24%. The large polarization does not depend on the excitation power as well as temperature, which can be used to exclude the possibility of extrinsic mechanisms related to the in-plane anisotropy. The observed optical anisotropy of $InAs/GaAs_{0.7}Sb_{0.3}$ QDs can be explained quite well in terms of the wave function overlap between electrons and holes across the heterostructure interface. Therefore, the emission reflects the intrinsic property of the orientation of chemical bonds at the type-II heterointerfaces. Our results shown here should be very useful to serve as a starting point for the study of the optical properties of other type-II semiconductor quantum dots.

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