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Influence of Thiol Coupling on Photoluminescence of Near Surface InAs Quantum Dots

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Photoluminescence (PL) of near surface InAs quantum dots (QDs) has been studied as a function of the distance to the surface (30, 20, 10, 6 nm). We observe a strong decrease in the QD PL intensity with decreasing barrier thickness. Nevertheless, the QDs still show reasonably strong PL intensity even when they are only 10 nm beneath the surface. After the deposition of self-assembled monolayers of octadecylthiol, we observe an increase in PL intensity up to a factor of 1.87. Such an enhancement is attributed to a decrease in the density of surface states. This demonstrates that near surface InAs QDs are very sensitive to changes of the surface conditions and the deposition of octadecylthiol monolayer may be used to increase their sensitivity, which is promising toward future bio-sensor applications.

Semiconductor nanostructures combined with biofunctional molecular composites are expected to play an important role in future sensor applications. Surface sensitive structures are needed and the semiconductor surface has to be rendered biocompatible for coupling to biological materials. One of the promising strategies for the surface engineering is based on supported lipid membranes on ultrathin polymer films [1]. In the first part of this paper we demonstrate that near surface InAs quantum dots (QDs) turn out to be well suited to indicate changes in the surface conditions. In such structures, nonradiative carrier recombination via surface states competes with radiative recombination detectable in a photoluminescence (PL) experiment. This may be used to investigate changes in the density of surface states. Recently, the electrochemical passivation of GaAs surfaces in aqueous electrolytes with self-assembled monolayers (SAMs) of octadecylthiol (ODT) has been reported [2]. Here we discuss effects of ODT monolayer deposition on the QD PL in air. An increase in the PL intensity is observed, suggesting the reduction of the surface states by the monolayer coating.

In Fig. 1a we show schematically the sample structure. A series of samples has been grown on semi-insulating GaAs (100)-oriented substrates using molecular beam epitaxy. After a GaAs buffer layer, a 15 period AlAs/GaAs superlattice (SL) was grown, followed by a 30 nm GaAs layer. The SL helps to confine the carriers in the near surface region even at room temperature. The InAs QDs [3–5] have been grown at 530 °C in Stranski-Krastanov [6] growth mode. The QDs are covered with an $Al_{0.33}Ga_{0.67}As$ layer

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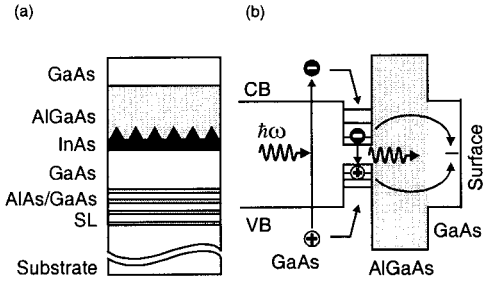

Fig. 1. a) A schematic of the sample structure. The InAs QDs are covered with an AlGaAs barrier of varying thickness. b) Radiative recombination competes with nonradiative recombination via surface states

of thickness 25, 15, 5 and 3 nm. This AlGaAs layer acts as a potential barrier to prevent carriers from diffusion to the surface and to suppress In segregation during growth of the dots [7]. Finally, the samples were capped with a thin GaAs layer.

The PL was excited by the 514 nm line of an Ar^+-laser with an excitation power of about 50 W/cm^2 (Fig. 2) and with a HeNe-laser at 633 nm with a lower excitation power of typically 20 W/cm^2 (Fig. 3). A liquid N_2-cooled InGaAs detector was used to measure the PL intensity dispersed by a 250 mm single grating spectrometer. PL measurements have been performed at 4.2 K and at room temperature.

PL spectra of InAs QD samples with decreasing distance (30, 20, 10, and 6 nm) of the QDs to the surface (shown in Figs. 2a and b) were measured at room temperature and at 4.2 K. For both temperatures we find a decrease in PL intensity with reduced barrier thickness and a shift of the emission maximum to lower energies. At room temperature (Fig. 2a) the energy separation between ground- and excited state is about 70 meV. The shift of the ground state emission maximum is 22 meV when varying the distance to the surface from 30 nm to 10 nm. The samples show strong PL signals up to a distance to the surface of 10 nm at room temperature. The sample with only 6 nm distance however shows no detectable luminescence, even for higher excitation powers. The observed decrease in the PL intensity with reduced barrier thickness may be explained by an increasing probability of nonradiative recombination of the

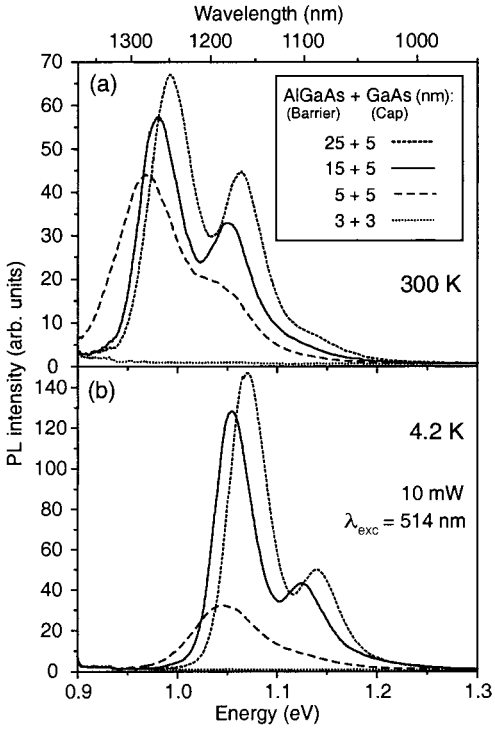

Fig. 2. PL spectra of near surface InAs QDs with decreasing AlGaAs barrier thickness (25, 15, 5, and 3 nm) measured at a) T = 300 K and b) T = 4.2 K. The PL intensity decreases in accordance with reduced barrier thickness. PL can be measured up to a distance of 10 nm to the surface

electron–hole pairs via surface states, as shown schematically in Fig. 1b. Radiative recombination competes with nonradiative recombination on the surface due to tunneling of carriers through the AlGaAs barrier. A decrease in barrier thickness results in increased probability for nonradiative recombination and, therefore, in a quenching of the PL intensity. Thermal activation of carriers over the barrier can be ruled out as the main escape process, because the spectra measured at 4.2 K (Fig. 2b) show similar decrease of PL intensity with reduced barrier thickness as the spectra measured at 300 K (Fig. 2a). For the sample with only 10 nm distance to the surface the decrease is even stronger pronounced at 4.2 K. To study the influence of the confinement potential in near surface structures, we have also performed PL measurements on InGaAs QDs and InGaAs QWs [8]. InGaAs QDs and InGaAs QWs showed an overall weaker PL intensity and an earlier quenching due to the lower confinement potential of those structures. Hence, we have chosen the InAs QD samples, with a considerably stronger PL intensity, to investigate the influence of surface functionalization on the PL.

The observed red-shift of the peak energy to lower energies with reduced distance of the QDs to the surface might have several reasons. Charge accumulation causes an electric field, resulting in a quantum confined Stark effect [9]. However, this effect is estimated to be not sufficient to explain a shift as large as 22 meV at room temperature (Fig. 2a). A similar red-shift has also been reported in Refs. [10] and [11] for InAs and InGaAs QDs, respectively. This spectral shift has been discussed in terms of changes of the strain, when the islands or QWs are covered only by a thin cap layer.

There have been many studies on the functionalization of GaAs surfaces with various sulfides and mercapto compounds in contact with air [12–14]. However, effects of the surface modification on the luminescence properties have been discussed in terms of increased PL intensity and PL decay time only for bulk GaAs [15, 16]. In previous studies, we demonstrated the electrochemical stabilization of the GaAs surface by the ODT monolayer deposition in aqueous electrolytes [2]. The ODT monolayers turned out to be stable even after more than one month in air [8].

The ODT monolayers were deposited self-assembling from the solution as reported previously [2]. Prior to the SAMs deposition, the cleaned InAs QD samples were dipped into concentrated HCl for 1 min. This surface pretreatment was chosen instead of the 'photochemical etching' procedure in order to minimize any uncertain effects that might be caused by the pretreatment. Indeed, the surface preparation did not result in any remarkable changes in the stability of the ODT monolayer in air [13]. The inset in Fig. 3b schematically shows the ODT coated sample structure.

In Fig. 3 we present PL spectra of InAs QDs with 25, 15, and 5 nm thick AlGaAs barriers, as grown and after ODT monolayer deposition. Note that the surfaces of the as grown samples were covered with native oxide. A strong increase in PL intensity is observed for each sample after the functionalization with ODT. Such an increase in PL intensity can be attributed to the reduction of the surface states resulting from the sulfur–arsenic coupling. Furthermore, we observe an additional spectral red-shift of 12 meV for InAs QDs which are closest to the surface. This may be explained, as discussed before, by a further reduced GaAs cap layer thickness.

In the inset in Fig. 3a we compare the increase in PL intensity of InAs QDs after functionalization for 10, 20, and 30 nm distance to the surface. The passivation factor P is defined as the ratio of PL peak intensity with and without ODT monolayers. The influence of surface modification is most pronounced for the samples with QDs in

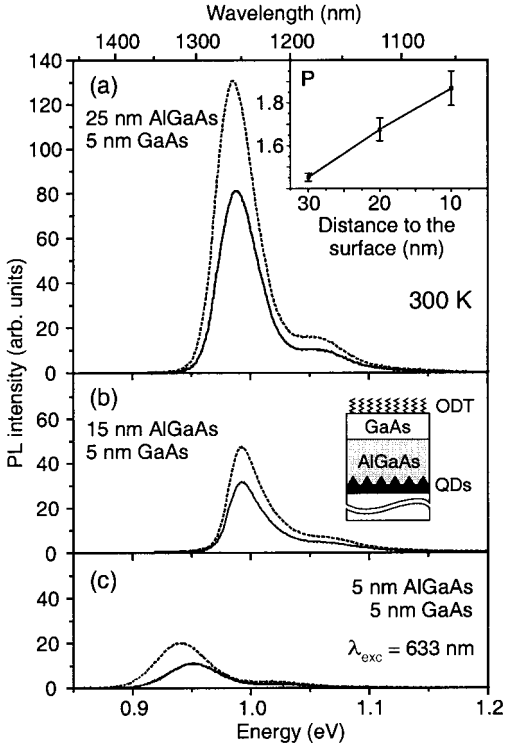

Fig. 3. PL spectra of near surface InAs QDs with (dashed line) and without (solid line) deposition of ODT monolayers. The AlGaAs barrier thickness is a) 25 nm, b) 15 nm, and c) 5 nm. The inset in a) shows the influence of ODT deposition on PL intensity as a function of the distance to the surface. The 'passivation factor' P is defined as the PL intensity with ODT divided by the PL intensity without ODT. The inset in b) shows schematically the ODT covered sample structure

closest proximity to the surface. We observe an increase in P from 1.45 to 1.87 by reducing the distance to the surface from 30 nm to 10 nm. As one can expect qualitatively, when the QDs are closer to the surface, they are more sensitive to the surface coupling reaction.

In conclusion, we performed PL experiments on near surface InAs QDs. Strong QD luminescence is observed even for the dots as close as 10 nm to the surface. The samples were functionalized by the deposition of ODT monolayers onto the GaAs surface. A significant enhancement of the PL signal (up to $P = 1.87$) was observed after SAM deposition, suggesting the reduction of the surface states by the sulfur–arsenic coupling. The obtained results demonstrate a promising potential not only to fabricate well-organized and biocompatible composites on GaAs, but also to detect changes in the surface conditions using near surface InAs QDs. This can be an essential step towards future applications in smart bio-sensors.

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