Shape Transitions of Self-Assembled PbSe Quantum Dots during Overgrowth

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Epitaxial overgrowth of self-assembled pyramidal PbSe quantum dots is shown to drastically affect their shape and composition due to anion exchange reactions. As shown by scanning tunneling microscopy, for PbTe capping layers this results in a complete truncation of the dots. Introduction of EuTe into the cap layer leads to an effective suppression of the anion exchange process. This preserves the original dot pyramids and induces a large stress concentration above the buried dots.

Introduction

Self-assembled semiconductor quantum dots are of great importance for optoelectronic devices. Their synthesis is based on the Stranski-Krastanow growth mode of lattice-mismatched heteroepitaxy in which 3D surface nanoislands spontaneously nucleate on a 2D wetting layer in order to relax the elastic energy of the system [1]. For practical device applications, these dots have to be covered by a protective capping layer in order to suppress surface oxidation as well as non-radiative carrier recombination. During this capping process, however, a strong redistribution of the dot material and alloying with the surrounding matrix takes place [2]. This changes the electronic and optical properties of the dots as well. In this work, we focus on the role of the chemical composition of the capping layer on the overgrowth process of self-assembled PbSe quantum dots. Using *in situ* scanning tunneling microscopy (STM), we reveal that an intricate interplay between intermixing and shape transitions occurs. While for pure PbTe overgrowth, a rapid dot dissolution and shape transition occurs, this effect is effectively suppressed by introduction of EuTe into the capping material and thus, the pyramidal structure of the native PbSe dots is preserved.

Experimental

The samples were grown by molecular beam epitaxy onto PbTe (111) buffer layers [3], [4]. Their structure consists of 5 monolayers (ML) PbSe dots followed by $Pb_{1-x}Eu_xTe$ capping layers with composition varying between $x_{Eu} = 0$ and 8% and thicknesses up to 200 Å. Identical growth conditions were used for all samples with a substrate temperature of 350 °C. Due to the -5.4% lattice-mismatch, PbSe dots are formed at a critical coverage of 1.5 ML, and at 5 ML the surface is uniformly covered by dots with a density of ~250 /μm^2. Immediately after growth, the samples were quenched and transferred to an attached UHV scanning tunneling microscopy chamber. Surface imaging was performed at a sample bias of 1 – 2 V and tunneling currents of 0.5 – 1 nA.

Results

Figure 1 (a) shows the 3D surface image of the initial uncapped PbSe islands, representing the starting condition for the overgrowth experiments. The as-grown dots display an average height of 110 Å and a base width of 280 Å, with a dispersion of ±12%.
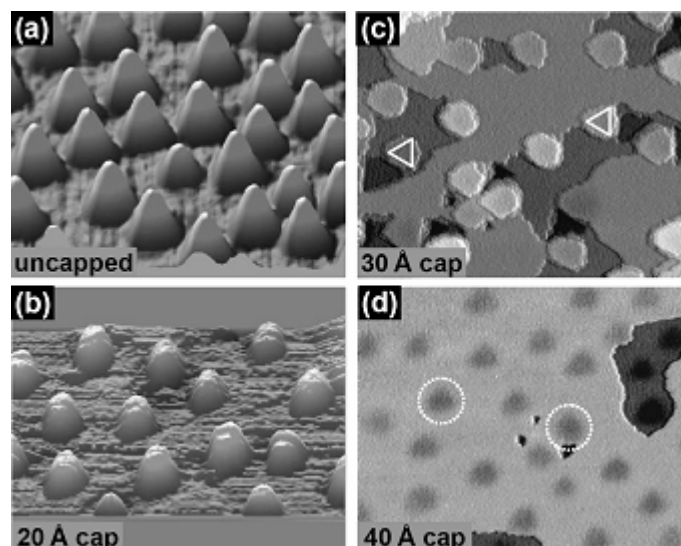

Fig. 1:   STM surface images (0.3 x 0.25 µm^2) of 5 ML PbSe dots covered with different PbTe cap thicknesses of 0, 20, 30 and 40 Å from (a) to (d), respectively.

All dots exhibit an identical pyramidal shape defined by three low-energy {100} side facets [3]. In the first set of experiments, the dots were capped with PbTe layers. As revealed by Fig.1, with increasing cap thickness a rapid shrinking of dot height and a transition in island shape occurs. Already after 20 Å PbTe deposition (Fig. 1(b)), the dots are transformed into truncated pyramids and their height is reduced to *half* of the original value. At 30 Å cap thickness (Fig. 1(c)), the surface has become almost completely flat with just the top 1 – 3 ML of the pyramid trunks still sticking out through the capping layer. Thus, the whole upper part of the dots has been completely dissolved. The flat top plateaus of the dots show a substantial rounding of the corners and a notably increased width compared to the original dot pyramids. Thus, the dot material has been redistributed towards the island edges. Further incrementing the cap thickness to 40 Å (Fig. 1(d)) renders a completely planarized surface with the usual 200 nm wide monolayer terraces typical for PbTe epilayers. In addition, evenly distributed shallow triangular surface depressions appear. Their density exactly matches the density of the buried dots and thus, they stem from the local lattice distortions induced by the dots.

A strikingly different surface evolution takes place when the dots are overgrown with $Pb_{0.92}Eu_{0.08}Te$ capping layers. This is demonstrated by the series of STM images displayed in Fig. 2. At 80 Å thickness (Fig. 2(a)), the PbSe pyramids still stick out through the cap layer and their tips remain visible even at 100 Å cap thickness (Fig. 2(b)). In addition, the apices of the dots retain the triangular shape of the pristine PbSe pyramids as evidenced by the enlarged STM images shown as inserts. Thus, the native PbSe dots are completely preserved and the deposited capping material just fills up the space between the islands. In addition, however, deep trenches remain at the perimeter of the dots, i.e., cap layer growth is strongly suppressed at the pyramid edges. The structure of the trenches consists of a ~200 Å wide denuded zone around the apex of the dots and additional holes at the pyramid corners. The depth of the trenches increases from 2-3 ML at 80 Å cap thickness to 5-8 ML at 100 Å cap thickness. As a re-

sult, the apices remain visible even at 120 Å cap thickness. As growth further proceeds, just one single ~10 ML deep hole is left above each island (Fig. 2(c)). The inner structure of these holes still displays the symmetry of the original PbSe dots. Only after further PbEuTe deposition, the holes start to be filled up such that at 160 Å a completely planar surface is regained (Fig. 2(d)). On the flat monolayer terraces again the signature of the dots in form of shallow triangular surface depressions appears.
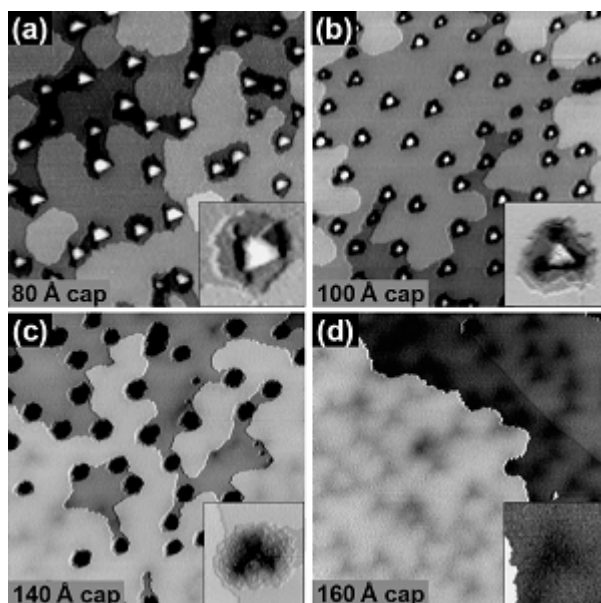

Fig. 2: STM images (0.5 x 0.5 µm^2) of 5 ML PbSe dots covered with Pb$_{0.92}$Eu$_{0.08}$Te cap thicknesses of 80, 100, 140 and 160 Å from (a) to (d), respectively. The enlarged images around single dots are shown as insert.
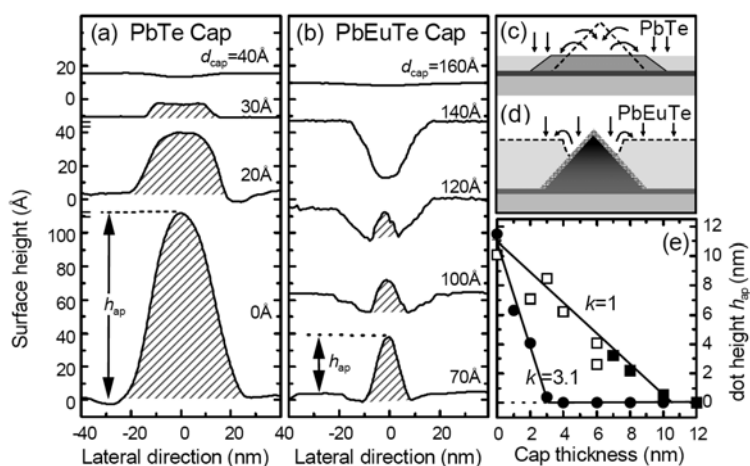

Fig. 3: STM surface profiles across PbSe dots capped with different PbTe (a) or PbEuTe (b) thicknesses d_{cap}. The shaded areas indicate the dot part extending above the cap surface. (e) Average apparent dot height h_{ap} plotted as a function of PbTe (●) and PbEuTe (■, □) cap thickness. The mechanisms determining the surface evolution are illustrated schematically in (c) and (d).

For a quantitative analysis, STM surface profiles were measured across the dots. The results are displayed in Fig. 3(a) and (b) for both sets of samples. For the PbTe case, the profiles show a rapid transition from sharp to truncated pyramids within 30 Å cap deposition. For the PbEuTe case, the island tips are preserved up to a cap thickness of 120 Å, and even at 140 Å deep holes are left on top of the islands that just reach to the bottom of the holes. The average apparent height hap of the dots indicated by arrows in Fig. 3(a) and (b) is plotted in Fig. 3(e) for PbTe (●) and PbEuTe (■) capping layers. As indicated by the solid lines, in both cases, the dot height decreases linearly with increasing cap thickness d, according to $h_{ap} = h_0 - k \times d$, where h_0 is the initial dot height and k is a scaling constant that characterizes planarization properties of the growth process. For usual thin film deposition, k is generally less than one, with the limiting case of k = 0 for conformal overgrowth. For PbEuTe capping, the fit of the experimental data yields a value of k = 1, representing the ideal case when growth takes place exclusively in between but not on top of the islands as shown schematically in Fig. 3(d). For PbTe overgrowth, k exceeds this value by as much as a factor of 3, indicating that the dissolution rate of the island tops is two times larger than the deposition rate. This dissolution is driven by strong intermixing between the dots and the capping material via anion surface exchange. Generally, intermixing is quite favorable in strained-layer heteroepitaxy because it effectively reduces the lattice-mismatch and thus, the total energy of the system. The reduced lattice mismatch, on the other hand, reduces the driving force for strain-induced coherent islanding [1]. Therefore, as the Se concentration at the top of the dots is reduced, the material starts to migrate towards the island edges to form more planar surface structures. This is illustrated schematically in Fig. 3(c).

Our model is supported by several control experiments. First of all, we find that PbSeTe ternary layers are stable against strain-induced coherent islanding when the Se concentration drops below a critical value of about 40%. Thus, intermixing indeed destabilizes the PbSe dots when the alloying is sufficiently large. Secondly, the characteristic shape transition is only observed for overgrowth but not during post growth annealing. This indicates that a direct exposure of PbSe with Te atoms is required for the dissolution process. Particular support comes from the dramatic effect of introduction of EuTe into the capping layer. This was clarified by an additional set of experiments which showed that predeposition of an intermediate EuTe layer as thin as 0.2 ML onto the PbSe islands before PbTe overgrowth is sufficient to completely inhibit the dot dissolution process. This is explained by the very large difference in binding energy of EuTe of 7.9 eV per atom pair compared to ~ 4 eV for the lead salt compounds, which drastically increases the energy barrier for surface exchange. This proves that atom exchange at the surfaces of the dots is the decisive mechanism for island dissolution.

Conclusion

In conclusion, overgrowth of self-assembled PbSe quantum dots induces pronounced shape transformations due to anion surface exchange reactions, leading to a significant shrinking of dot height and rounding of shape. This process can be suppressed by introduction of a barrier layer by which the pyramidal structure of the native dots is preserved. This demonstrates that the cap layer composition is an effective means for tailoring the structure of self-assembled quantum dots as required for device applications.

Acknowledgements

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