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Growth of ZnSe nanowires by molecular beam epitaxy

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***Abstract* — We have grown ZnSe nanowires on Au-coated SiO_2 by molecular beam epitaxy. Data are reported for structures grown at 450 and 550 °C. High resolution electron microscopy shows that the lower growth temperature gives rise to a higher density of high-quality nanostructures and that nanowires, nanobelts and nanosaws are all present in our samples. ZnSe nanostructures do not grow on the non-coated substrate. Photoluminescence shows a blue component in samples grown at lower temperature.**

***Index Terms* —Electron microscopy, Epitaxial growth, Nanotechnology, Photoluminescence, Semiconductor materials.**

I. INTRODUCTION

One-dimensional semiconducting nanostructures have become very popular in recent years both for fundamental physics and their potential applications in electronic and optoelectronic devices [1]. Several methods have been proposed for the synthesis of single-crystal nanowires (NW), such as laser ablation, high-temperature thermal evaporation and plasma-enhanced chemical vapour deposition [2,3]. In most cases, a metallic catalyst allows the growth of one-dimensional structures.

Molecular beam epitaxy (MBE) is a very effective method to grow heterostructures with very sharp interfaces. Single electron transistors and resonant tunnelling devices have been demonstrated with III-V semiconductor nanowires using this growth technique [4,5].

NWs based on II-VI compounds are suitable candidates for applications in nano-optics. ZnSe has been extensively studied as a material for blue-light emitting devices, but only few reports are found in literature on the synthesis of ZnSe NWs. The MBE growth of ZnSe NWs on GaP(111) substrates has been reported by Chan et al. [6]. They proposed 530°C as the lower limit for gold-catalysed nucleation because Au nanoparticles were transformed into molten state at that temperature. Using metal-organic chemical vapour deposition and Ag as catalyst, Zhang et al. [7] achieved a growth temperature of 450°C, but the absence of any silver particle at the edges of their wires suggests that a more complicated growth mechanism may occur.

Here we report the MBE growth of ZnSe nanostructures at 450°C and 550°C using gold as catalyst. Transmission electron microscopy shows the coexistences of nanobelts and nanosaws together with thin and straight nanowires. Photoluminescence (PL) in the blue region has been observed from samples with a high-density of NWs.

II. EXPERIMENTAL

All samples were grown by a solid-source MBE. A 100nm-thick SiO_2 layer was sputtered on n-doped Si wafers, and the substrates were then coated with a thin (2nm) Au film before being loaded into the growth chamber. Elemental Zn and Se were evaporated on the sample surface for 1h, with fluxes corresponding to a 2D growth rate of 0.45 μm/h. The VI/II beam-equivalent-pressure ratio was 2.5. The growth temperatures (T_g) were 450 °C and 550 °C. The structural and optical properties of the resulting ZnSe nanostructures are investigated by field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM, 400KV), Raman spectroscopy, and photoluminescence. PL was measured at 10 K by shining 1mW on the sample from an Ar^+ laser operating in the UV (333.6-363.8 nm).

III. RESULTS AND DISCUSSION

Fig. 1 shows a FE-SEM plan-view image for two representative samples grown at T_g =450°C (a) and at T_g=550°C (b), respectively. The lack of nanostructures where gold was mechanically removed prior to ZnSe deposition proves the key role of the catalyst for the nucleation. While only few NWs are found on the high-temperature sample, their density increases when the temperature is lowered to 450°C. In this case, large quantities of randomly oriented NWs, up to several microns in length, arise from the gold-coated zones and extend to the surrounding areas. Some agglomerates are

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still observable in the background of the wires shown in Fig. 1(a), pointing to the simultaneous occurrence of two competing nucleation processes.

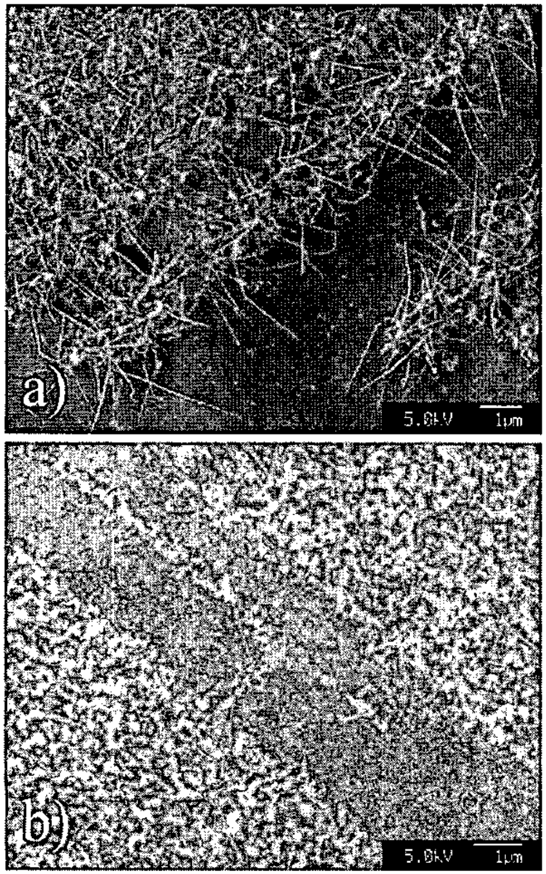

Fig. 1. FE-SEM images of samples grown at (a) T_g=450°C and (b) 550°C. No growth of nanostructures is observed where Au is removed from the substrate.

Bright-field TEM micrographs of the ZnSe nanostructures formed at T_g=450 °C are plotted in Fig. 2(a,b). Fig. 2(a) shows a 20 nm-diameter Au particle on top of a straight NW. Its size matches the wire diameter, as expected for catalyst-enhanced growth. NWs with a diameter of ~15-30nm represent about 20% of the overall nanostructures deposited at 450 °C. A smaller fraction of nanosaws (10%), such as those in Fig. 2 (b,c), is also seen. Most of the high-aspect ratio nanostructures (50%) are found to be nanobelts with diameters in the 50-60 nm range. The remaining portion is mainly due to wide, kinked, and short low-quality NWs. No gold particle is seen by TEM in the case of nanobelts and nanosaws, suggesting that other growth mechanisms might be responsible for their nucleation.

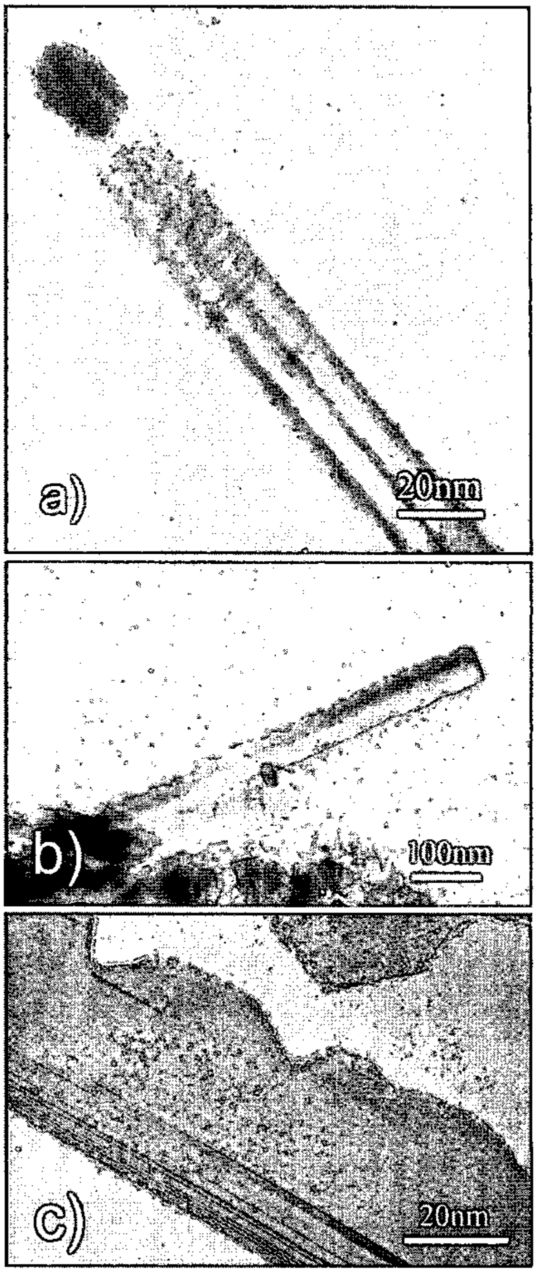

Fig. 2. TEM images of nanostructures present in the 450 °C sample. a) Straight NW showing the Au catalyst on the top; b) a nanosaw; c) high-resolution image of the nanosaw shown in b).

Other II-VI materials such as ZnO, CdSe and ZnS have been reported to give rise to self-assembled crystals of intriguing shape, even in the absence of any catalyst particle [8,9]. The growth mechanism of nanosaws deserves particular attention since it paves the way for the self-assembly of complex structures by exploiting the intrinsic properties of the crystal planes matching. Our results are the first report of ZnSe nanosaws. The comparison of our data with refs. 8-9 suggests that the percentage of each nanostructure strongly depends on the growth technique and growth parameters. The challenge still lies in the controlled production and selective placement of each kind of structure.

The HRTEM image in Fig. 2(c) shows a highly crystalline nanosaw of about 34 nm diameter. The height of the saw tooth ranges between 8 and 10.5 nm. The lattice fringes correspond to the (111) planes of ZnSe. Large angle grain boundaries are incorporated in the structure of the nanosaw and run parallel to the saw axis. These are both at the top, where they are involved in the formation of the saw tooth, and at the bottom, where misoriented layers of different thickness give rise to the "stripy" contrast of Fig. 2(c). The outer surface of the nanosaw shows an amorphous-like contrast, suggesting partial oxidation of the first few surface layers.

The photoluminescence spectra taken at 10 K are reported in Fig. 3 for both samples. They show different emissions. Whilst the sample grown at high temperature has an unique broad green band centred at about 2.25 eV, the sample grown at low temperature shows a more complex spectrum which includes a blue emission doublet at 2.68 and 2.77 eV. All the bands seen at low T in both samples are still observable up to room temperature.

Previous measurements on ZnSe NWs grown using Au as a catalyst [10] have shown green luminescence. This was attributed to a recombination between free electrons and holes trapped on the Au acceptor [10]. Cathodoluminescence of ZnSe NWs, obtained using Ag as the catalyst, showed blue emission at 2.68 eV with no evidence of luminescence degradation due to Ag incorporation [7].

Our observation of blue luminescence from the sample grown at 450 °C could be interpreted as a signature of high quality ZnSe structures. Further work is needed to understand the origin of the observed recombinations and to uniquely assign them to specific structures observed by electron microscopy.

Raman spectroscopy allows probing the structure and diameter of nanowires [11]. We detect a broadening and downshift of the ZnSe LO and TO phonons compared to bulk material (not shown here). This confirms the presence of ZnSe nano-crystals in the sample.

IV. CONCLUSION

The growth of ZnSe nanowires by MBE on Au-coated SiO_2 has been demonstrated. A growth temperature as low as 450 °C gives a high density of high-quality one-dimensional nanostructures, which include nanowires as well as nanosaws and nanobelts. Intense luminescence including a blue component is observed from this sample.

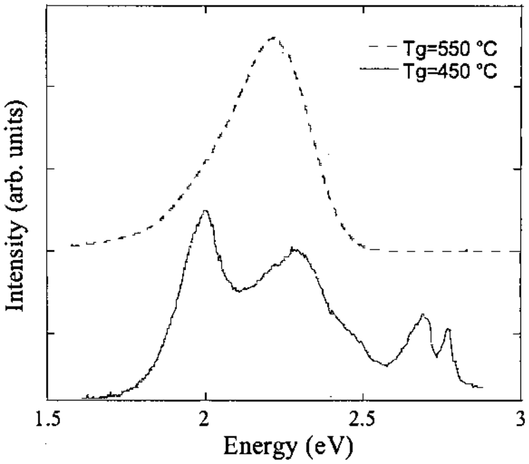

Fig. 3. Photoluminescence spectra measured at 10K.

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