

Atomic layer deposition of ZnSe/CdSe superlattice nanowires

R. Solanki,^{a)} J. Huo, and J. L. Freeouf

Department of Electrical and Computer Engineering, OGI School of Science and Engineering, Beaverton, Oregon 97006

B. Miner

Intel Corp, Hillsboro, Oregon 97124

(Received 19 July 2002; accepted 24 September 2002)

Atomic layer deposition has been employed to grow nanowires composed of ZnSe/CdSe superlattices. Growth of the nanowires was initiated using gold nanoparticles and the vapor-liquid-solid mechanism. High-resolution transmission electron microscopy shows that these structures are single crystals and the phase of alternating layers of ZnSe and CdSe is zinc blende. The (111) planes of ZnSe and CdSe are oriented at 60°. © 2002 American Institute of Physics. [DOI: 10.1063/1.1521570]

One-dimensional nanoscale wires and tubes have lately been attracting considerable attention due to their electrical and optical properties. Although most of the work to date has been concentrated on synthesis of homogeneous structures or heterojunctions, realization of one-dimensional compositionally modulated heterostructures is generating a great deal of interest for potential nanoelectronics and photonic applications. To date synthesis of nanowires composed of modulated III-V and group IV elements has been demonstrated mostly using laser assisted growth.^{1,2} Below we describe our initial results of growth of ZnSe/CdSe heterostructure nanowires using atomic layer deposition (ALD). These direct and wide band gap compounds have been of interest for producing laser action in the blue-green spectral range. Hence, this combination of materials presents an intriguing system of producing excited carriers in radial confinement. We also show below that ALD is an ideal method for growth of superlattices in one dimension in a controlled fashion.

Atomic layer deposition is a monolayer stepwise growth process that proceeds by exposing the substrate surface alternately to each precursor followed by an inert gas (nitrogen) pulse to remove the excess species and by-products of the reaction. Therefore, unlike chemical vapor deposition, in ALD each precursor is introduced to the substrates separately. Hence, with this sequential mode, the duration of each exposure is adjusted so that each surface reaction goes to completion before starting the next reaction. Under properly adjusted experimental conditions all the surface reactions are saturated, making the growth process self-controlled. Therefore, one of the main differences between laser assisted growth that has been reported for nanowire growth and our approach (ALD) is the self limited surface reaction. The self-limited reaction of ALD allows better control for depositing films with monolayer thickness. The film thickness can be determined accurately by the number of deposition cycles. In addition, the separate dosing of precursors assures that no detrimental gas-phase reactions will take place.

There are several reports of initiating nanowire or nanofiber growth using a metal catalyzed process.¹⁻³ In our

case, monodispersed gold nanoparticles were employed together with the vapor-liquid-solid process.⁴ The deposition temperature was selected such that the first precursor (Zn) introduced into the reactor formed a eutectic with gold. The Zn-Au eutectic temperature is within our deposition conditions described later.⁵ Following nucleation in the eutectic region, these structures solidify away from the Au interface.

The substrates for this investigation consisted of 2 in. × 2 in. silicon wafer pieces with a 100-nm-thick layer of SiO₂ and bare 2 in. diameter GaAs wafers. Before loading these substrates in the ALD reactor, they were treated for 1 min with 0.1% solution of poly-L-lysine and then to a gold-nanocluster solution (average nanoparticle size of 6 nm), followed by a de-ionized water rinse. The adhesion of the Au particles was confirmed using an atomic force microscope. The precursors for ZnSe and CdSe were elemental Zn, Se, and Cd. Initially, thin films of ZnSe and CdSe were grown on GaAs substrates to optimize the deposition parameters and to confirm that we were operating in the ALD window to produce monolayer growth per cycle. One cycle for ZnSe growth consisted of a 0.14 s pulse of Zn, then 0.2 s pulse of N₂, followed by 0.2 s pulse of Se, and finally another 0.2 s pulse of N₂. For CdSe growth, the Zn pulse was replaced with a 0.4 s pulse of Cd. Substrate temperature ranged from 400 to 420 °C. The composition of the nanowires was varied by changing the number of cycles of each component. For example, a sequence that consisted of ten cycles (which corresponds to ten monolayers) of ZnSe was followed by five cycles (five monolayers) of CdSe was repeated 100 times. By increasing the number of cycles, nanowires or fibers over a micron long were grown. This illustrates the high degree of flexibility that can be achieved with monolayer growth control capability of ALD. Details on ALD growth of ZnSe and CdSe quantum wells were reported previously.⁶

Optical microscopy, of course, is unable to verify sizes on the order of 6 nm. However, confirmation of nanowire growth and qualitative information on these structures was obtained by means of fluorescence microscopy. Since we could clearly observe photoluminescence from these structures, this technique provided us with a quick test. Two excitation sources for photoluminescence were available by us-

^{a)}Electronic mail: Solanki@ece.ogi.edu

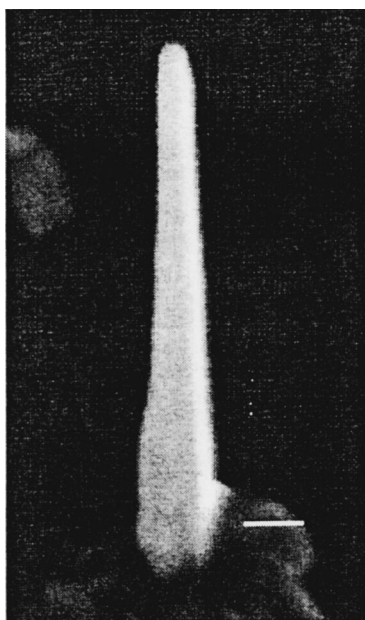


FIG. 1. SEM view of a ZnSe/CdSe nanowire. The scale bar is 5 nm long.

ing filters of either blue light (wavelength 450–490 nm) or green (540 nm). In the case of ZnSe (band gap $E_g \sim 2.8$ eV) light of 450 nm can excite electron hole pairs, but light of substantially longer wavelength cannot. Indeed, it was observed that we could not obtain photoluminescence using 540 nm photons. However, the band gap of CdSe ($E_g \sim 1.84$ eV) is much smaller, and can easily be excited by either 450 nm or by 540 nm photons. The photoluminescence excited by 450 nm photons ranged in appearance from white to yellow to red. CdSe-containing samples also provided red luminescence when excited by 540 nm photons. At this time we are uncertain of the origin of the various colors observed from the luminescence, however, in the future we expect to have equipment to do spectroscopic analysis. These results clearly confirmed that growth occurred and that it was localized in spots. We also established that in most cases the growth occurred vertically to the surface, because the light origin extended over a vertical range exceeding the depth of focus of our microscope.

A scanning electron microscope (SEM) provided a more detailed look at the nanowires. A SEM view of a typical nanowire grown on a Si/SiO₂ surface is shown in Fig. 1. These nanowires have a wider base, then taper down. The reason for the wide base could be due to the initial conformal coating of the Au nanoparticle by ALD. In case of long nanowires (1–2 μm), there is a wide base followed by a narrowing and then they maintained a uniform diameter over most of their length. In these long nanowires, a distinct tapering is observed at the free end, similar to that observed in metal organic chemical vapor deposited nanowires.⁷ Also, the direction of the nanowire growth is not always normal to the surface.

These structures have facets, indicating single crystal growth. This was confirmed by high-resolution transmission electron microscopy (HRTEM) shown in Fig. 2. The fiber in this case was composed of 15 monolayers of ZnSe and five monolayers of CdSe. Lattice image of the fiber shows the

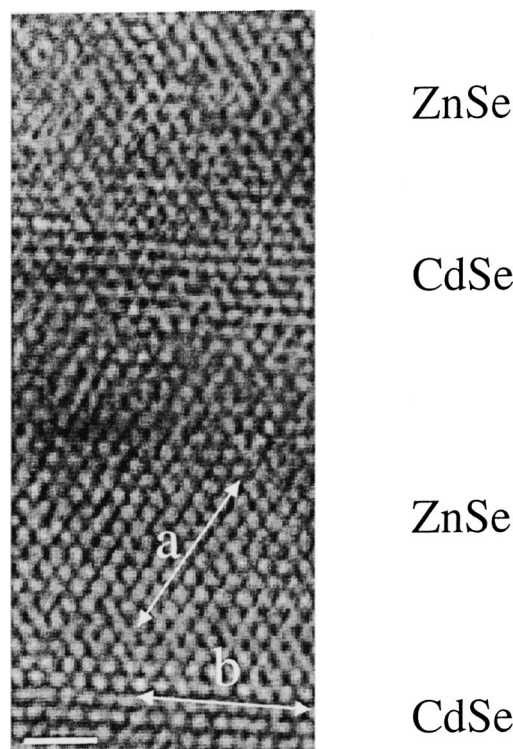


FIG. 2. HRTEM showing ZnSe/CdSe superlattices. The inset arrows indicate the direction of (111) planes of ZnSe(a) and CdSe(b). The scale bar is 1 nm.

orientation of (111) planes of ZnSe (inset a) and (111) planes of CdSe (inset b). From the lattice image we measured the d spacing of ZnSe (111) to be about 3.3 Å and that of CdSe (111) to be about 3.5 Å. The measured d space also matches the data from Fourier transform image.

We know that for cubic crystal structures, $d(hkl) = a/(h^2 + k^2 + l^2)^{1/2}$, where d is the distance between (hkl) planes, (hkl) is the index of planes and a is the lattice constant. According to Ref. 8, ZnSe has a zinc-blende structure with $a = 5.67$ Å and CdSe with a zinc-blende structure has $a = 6.05$ Å. Calculating the d -spaces with the earlier equation and lattice constant a values, we determined $d(111)_{ZnSe} = 3.27$ Å and $d(111)_{CdSe} = 3.49$ Å. The calculated values agree with the measured values very well. Also, the angle between CdSe(111) and ZnSe (111) planes was measured to be 60°. It is interesting to note that the fiber growth occurs in the [111] direction of CdSe.

The composition of these structures was examined using energy dispersive x ray (EDX). This is shown in Fig. 3 where

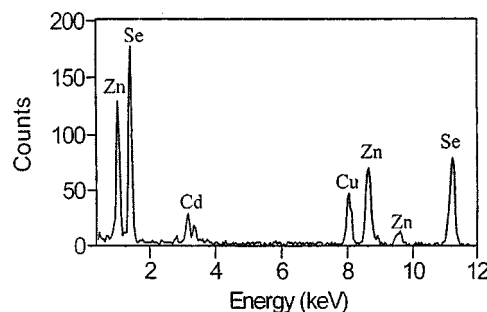


FIG. 3. EDX spectrum showing the composition of the superlattice nanowire.

the main components are Zn and Se. A smaller Cd peak is also observed. The Cu signal originates from the copper TEM grid. An EDX scan of these fibers did not show a clear composition modulation probably due to the relatively large electron beam spot size. Electron flight simulation showed an effective electron-materials interaction diameter of 4 nm, compared to 1.5 nm width of the five CdSe layers.

In summary, we have shown that ALD can be used to produce nanowires composed of ZnSe/CdSe superlattices. These wires or fibers are single crystal and are comprised of alternating layers of (111) oriented ZnSe and CdSe. The (111) planes of ZnSe and CdSe are oriented at 60° with respect to each other. Although this work describes growth of group II–VI nanowires, ALD can be employed for growth of nanowires composed of a wide range of materials with monolayer thickness control.

The authors wish to acknowledge helpful discussion with Professor Shankar Ranavare, Professor Jack McCarthy, and Professor John Carruthers.

- ¹M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith, and C. M. Lieber, *Nature (London)* **415**, 617 (2002).
- ²Y. Wu, R. Fan, and P. Yang, *Nano Lett.* **2**, 83 (2002).
- ³M. K. Sunkara, S. Sharma, R. Miranda, G. Lian, and E. C. Dickey, *Appl. Phys. Lett.* **79**, 1546 (2001).
- ⁴R. S. Wagner, in *Whisker Technology*, edited by A. P. Levitt (Wiley, New York, 1970), p. 47.
- ⁵M. Hansen, *Constitution of Binary Alloys* (McGraw Hill, New York, 1958), p. 241.
- ⁶R. Engelmann, J. Ferguson, and R. Solanki, *Appl. Phys. Lett.* **70**, 411 (1997).
- ⁷T. Shimada, K. Hiruma, M. Shirai, M. Yazawa, K. Haraguchi, T. Sato, M. Matsui, and T. Katsuyama, *Superlattices Microstruct.* **24**, 453 (1998).
- ⁸A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972), p. 9.