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ScienceDirect
Solid State Communications 141 (2007) 635–638
solid state communications
www.elsevier.com/locate/ssc

Femtosecond laser-induced ZnSe nanowires on the surface of a ZnSe wafer in water

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Received 2 August 2006; received in revised form 11 December 2006; accepted 20 December 2006 by P. Sheng
Available online 7 January 2007

Abstract

We present a simple route for ZnSe nanowire growth in the ablation crater on a ZnSe crystal surface. The crystal wafer, which was horizontally dipped in pure water, was irradiated by femtosecond laser pulses. No furnace, vacuum chamber or any metal catalyst were used in this experiment. The size of the nanowires is about 1–3 μm long and 50–150 nm in diameter. The growth rate is 1–3 μm/s, which is much higher than that achieved with molecular-beam epitaxy and chemical vapor deposition methods. Our discovery reveals a rapid and simple way to grow nanowires on designed micro-patterns, which may have potential applications in microscopic optoelectronics.

PACS: 81. 05.Ys; 61. 80. Ba

Keywords: A. Nanowire growth; B. Laser ablation; C. Crystal structure

1. Introduction

ZnSe is an important wide band-gap (2.8 eV) semiconductor with potential applications in short-wavelength optoelectronic devices. Since control of the size and dimensions can lead to special optical and electronic properties, many studies have been focused on the fabrication of various ZnSe nanostructures [1–3]. Several groups reported recently the growth of semiconductor nanowires with molecular beam epitaxy (MBE) [4,5], chemical vapor deposition (CVD) [6], thermal evaporation process (TEP) [7,8] and pulsed laser deposition (PLD) methods [1,9]. These methods are usually rather complicated. The powder and the substrate are put into a furnace, and mounted in a vacuum chamber. Then they are heated to a special temperature at a certain rate, while the vacuum chamber has to be kept at a designated pressure. Moreover, gold, iron and silver are usually used as catalysts to enhance the nanowire growth. In order to grow nanowires on the designed pattern, the corresponding masks have to be made in advance and covered on the substrate surface. Furthermore, the experiments usually last for several hours. It is an important research topic to grow nanowires with a simple and rapid method [5–10].

Femtosecond (fs) laser ablation and microprocessing have been studied intensively in the last decade [11–16]. Nanoparticles, nanospikes and nanogratings have been fabricated by this method [16–19]. It was reported recently that ZnO nanowires were fabricated using a fs laser to ablate the precursors [20]. The obtained crystalline nanowires were very uniform in diameter. This was attributed to the nonthermal ablation of the precursor materials by the fs laser, which can induce the formation of uniform nanoparticles. In this paper we report a simple method for rapid growth of ZnSe nanowires on a ZnSe crystal surface irradiated by a fs laser.

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doi:10.1016/j.ssc.2006.12.025

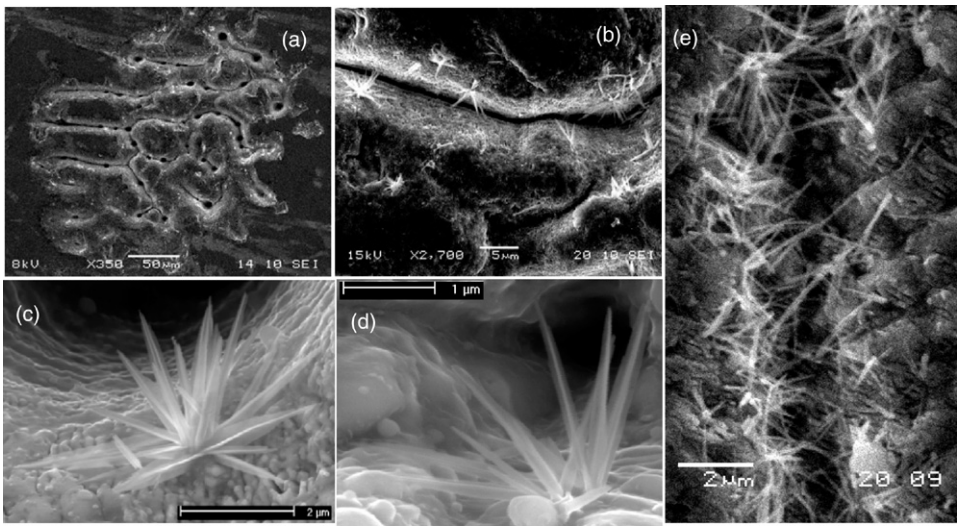

Fig. 1. SEM images of the ablation crater and ZnSe nanowires. The laser parameters were: (a)–(c) 800 nm, 220 μJ and 2000 pulses; (d) 400 nm, 18 μJ and 1500 pulses; (e) 800 nm, 80 μJ and 1 kHz.

2. Experimental section

A commercial Ti:sapphire regenerative amplifier (Hurricane, Spectra-Physics) was used to generate a p-polarized 800 nm laser pulse with 130 fs, 0.7 mJ at 1 kHz repetition rate [19]. The laser frequency was doubled through a beta barium borate (BBO) crystal, and the polarization was adjusted with a quarter-wave plate. The laser pulse energy was continuously changed by a Glans polarizer. Finally, the laser went through a silica lens (250 mm focus), and irradiated vertically down to the upper surface of a ZnSe wafer. The wafer was undoped single-crystal with both surfaces polished optically, and no metal catalyst was deposited in advance. The sample was horizontally dipped to a depth of 1.2 mm in pure water in a glass beaker. The beaker was mounted on a five-dimension translation stage. The experiments were conducted in air. After laser ablation, the sample was rinsed in acetone, ethanol and deionized water in sequence, and cleaned with an ultrasonic cleaner for 5 min. The nanowires were measured with a scanning electron microscope (SEM) and a transmission electron microscope (TEM) (JEOL 2010F, 200 KV).

3. Results and discussion

During laser ablation of ZnSe crystal, the water near the laser focus is broken down and "boiled". As the laser transmits through the "boiled" region, it is defocused and split into filaments. Therefore, the ablation crater is larger than 100 μm in diameter, and there are many micro-holes and grooves on it [see Fig. 1(a)]. Fig. 1(b) and (c) show the enlarged views of a groove and a group of nanowires, respectively. Pine-needle nanowires usually grow on the side walls of micro-grooves and holes. Their sizes are 0.5–3 μm long and 50–150 nm in diameter. Fig. 1(d) presents a group of nanowires induced by a 400 nm laser. When the sample is translated at a speed of 104 mm/min, an ablation groove with a width of 5 μm can be fabricated on the sample surface. There are many nanowires grown on the groove [see Fig. 1(e)]. The laser parameters were 800 nm, 80 μJ and 1 kHz, and the focal length of the lens 100 mm. Using this method, we can easily grow nanowires on a designed micro-pattern without polluting or damaging the neighboring area.

The ZnSe nanowires were scraped off with a stainless steel needle, and their structure analyzed by TEM. A TEM image of a nanowire is presented in Fig. 2(a). It is about 120 nm in diameter with a smooth sidewall. Fig. 2(b) and (c) show the high-resolution TEM (HRTEM) image and the Fourier transform of the square part, respectively. The lattice space indicates that the nanowires are wurtzite single crystal growing along the *a* axis. The ZnSe nanowires reported to date usually have a zinc blende structure growing along the (111) direction [6]. Wurtzite ZnSe nanowires growing along the *c* axis were recently fabricated with PLD and thermochemical methods [9,21]. Nanowires with a wurtzite structure can also grow rapidly along the *a* axis. ZnO is very similar to ZnSe, which is also a II–VI group semiconductor with wurtzite structure and wide bandgap (3.1 eV). Several groups have reported ZnO nanowires growing along the *a* axis [22, 23]. Fig. 2(d) shows an energy dispersive x-ray spectrograph (EDXS) of the nanowires prepared in this study, which indicates that the molar ratio of zinc to selenium is nearly 1:1. Since no metal catalyst was used in our experiments, the nanowires are thus quite pure.

Fig. 3 shows the growth process of the nanowires. Nanowires begin to nucleate and grow after the sample is irradiated by 100 laser pulses (see Fig. 3(a) and (b)). Their lengths increase linearly to 1.7 μm as the pulse number increases to 1500 (see Fig. 3(c)). The growth rate is 1.2 nm/pulse. However, if the pulse number increases further, the length of the nanowires begins to decrease slowly (see Fig. 3(d)). This is because the laser ablation of the ZnSe crystal surface and the deposited nanoclusters induce the growth of nanowries, while the laser can also ablate the nanowires and cut down their lengths. The nanowires are longest and most uniform for the crystal wafer irradiated by 1500 laser pulses. When the 800 nm laser pulse number is fixed at 700, we find that nanowire lengths are