Low-temperature growth and Raman scattering study of vertically aligned ZnO nanowires on Si substrate

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High-density ZnO nanowires (ZnONWs) were aligned onto Au-catalyzed Si substrate through a simple low-temperature physical vapor deposition method. Scanning electron microscope (SEM) observations, x-ray diffraction (XRD) analysis, and photoluminescence spectra showed that the ZnONWs were single-crystalline, with a hexagonal wurzite structure. All of the results inferred from the SEM observations, the XRD rocking curves, and the Raman spectra for the investigated samples confirm that the ZnONWs are well aligned and *c*-axis oriented. The Raman spectra also indicated that the ZnONWs on Si substrates are under the biaxial compressive stress. Since it takes the advantage of low-cost, easily controlled deposition spot (due to the selective deposition trait of the Au layer), potential for scale-up production, and ability to integrate with Si substrate, this technique has a potential in future for fabricating the ZnONW array-based optoelectronic devices. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1630849]

Significant advances in the areas of wide-bandgap semi-conductor nanowires (NWs) growth and fabrication with well-defined configuration have been achieved over the past few years.[1] Yang's group pioneered the study of optically pumped UV lasing from epitaxially grown ZnONW arrays on sapphire substrates (880 °C).[2] Kim *et al.* reported that single-crystal GaN nanorod arrays could be grown on the sapphire substrate via the hydride vapor-phase epitaxy technique.[3] Nevertheless, sapphire is not conductive and also relatively expensive. This may pose a serious limitation on the applications of the nanowire arrays in optoelectronic devices. In the pursuit of the next-generation semiconductor NW-based optoelectronic nanodevices, it would be highly desirable if well-ordered nanowires can be directly aligned on a conductive and low-cost substrate, such as a Si wafer. Unfortunately, the large mismatches in the thermal expansion coefficients and the lattice constants would introduce rather large stress between the ZnO (GaN) and the Si wafer. Moreover, this stress is easily aggravated at high temperature. Many previous efforts in preparing the well-oriented ZnONW arrays on the Si wafer have not reached satisfactory quality because of the large stress at high growth temperature as well as their chemical dissimilarities.[4]

We believe that deposition of high-quality and well-aligned ZnONW arrays on the Si substrates can be achieved by an appropriate selection of the nucleation catalyst and the growth conditions. In a previous letter, we reported the field emission properties from well-aligned ZnONWs grown on a Si wafer at a considerably low temperature of 450 °C.[5] A sol–gel method was applied to deposit Co nanoparticles on the Si wafer as metal catalyst to initiate the vapor–liquid–solid (VLS) growth of the ZnONW arrays. However, this wet-chemistry method may cause a pollution problem on the semiconductor samples and may also be incompatible with the conventional semiconductor fabrication techniques. In this letter, we report that well-aligned ZnONW arrays were fabricated on the Au-coated Si wafers via vaporizing the metal Zn powders at the low growth temperature of 500 °C. The Raman scattering characteristics of the as-grown *c*-axis-oriented ZnONW arrays were also studied at length.

Synthesis of the ZnONW arrays was carried out in a conventional furnace with a horizontal alumina tube. In a typical process, an Au layer of 2 nm in thickness was first thermally evaporated onto the polished side of a Si (100) wafer to serve as catalyst. The Au-coated side was faced downward on an alumina boat loaded with the Zn powder (purity: 99.999%), at a separation of about 5 mm. The alumina boat was then transferred into the center of the tube furnace. Afterwards, the chamber was heated up to 500 °C at a rate of 20 °C/min under a constant flow of Ar (99.9%) of 200 sccm and kept for 5 h. After cooling down, a white deposition layer was found over the Au-coated Si wafer. The as-synthesized products were characterized by scanning electron microscopy (SEM) [Amray FEG-1910] and x-ray diffraction (XRD) [X'pert™ MRD-Philips diffractometer]. To investigate the crystal orientation, a XRD rocking curve was taken. The photoluminescence (PL) spectra were obtained with a He-Cd laser of 325 nm wavelength and measured at room temperature. The Raman scattering was performed in the near backscattering geometry using an Ar$^+$ laser with a power of 20 mW. The scattered radiation was analyzed with a double monochromator and detected with a liquid-nitrogen-cooled charge-coupled device.

In order to identify the crystal phase of the deposited materials, samples were analyzed by XRD. The spectrum [Fig. 1(a)] reveals that the as-synthesized products are the

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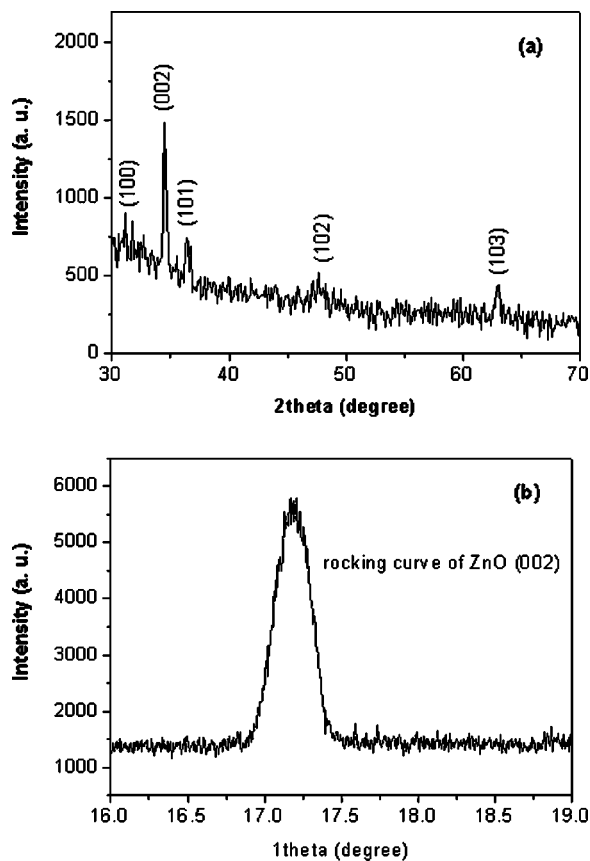
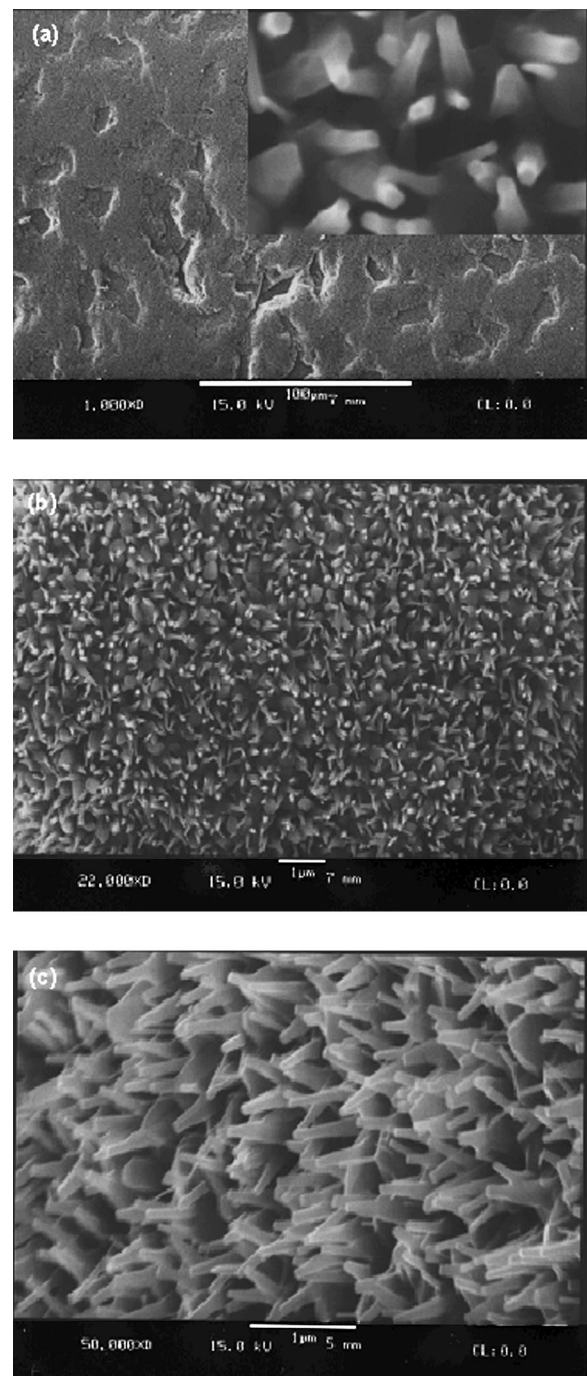FIG. 1. (a) XRD spectrum of ZnONW arrays on Si (100) substrate. (b) The x-ray rocking curve of ZnONW arrays [(002) plane].

FIG. 2. SEM images of well-aligned ZnONWs grown on Si substrate. (a) Low magnification image; bar: 100 μm. Inset: magnified image of well-aligned ZnONWs; bar: 1 μm. (b) High-density well-aligned ZnONWs; bar: 1 μm. (c) The image of ZnONW arrays from an oblique view angle, bar: 1 μm.

hexagonal wurzite ZnO with lattice constants of $a = 3.24$ Å and $c = 5.20$ Å. The SEM images (Fig. 2) show that the high density nanowires are vertically aligned to the Si substrate with a film-like morphology [Fig. 2(a)]. The diameters of the nanowires are in the range of 70 to 100 nm, with lengths of several micrometers. In the inset of Fig. 2(a), it is illustrated that some of the NWs' tips have the hexagonal facets. This implies that the one-dimensional (1-D) growth is directed along the c axis. Figure 1(b) demonstrates that the full width at half-maximum of the x-ray rocking curve of the (002) peak is as narrow as 0.28°. This provides further statistical evidence that the nanowires are indeed vertically oriented on the Si wafer preferentially with the (002) plane parallel to the Si substrate, namely, these nanowires are grown along the c-axial 1-D growth direction, which can be explained by the well-known VLS growth mechanism.[6] One notes that the oxygen taking part in the process of the ZnO crystal formation comes from the residual oxygen in the apparatus.

Low growth temperature is beneficial to acquire the well-aligned ZnONWs on the Si substrates, in that the stress between the ZnONWs and the Si substrate is reduced substantially at low growth temperature. Experimental results demonstrate that well-aligned ZnONW arrays are obtained at 500 °C, while only randomly distributed ZnONWs were formed the growth temperature higher than 550 °C.

The space group of the hexagonal wurzite ZnO belongs to C_{6v}^4, with two formula units per primitive cell. According to the group theory, single-crystalline ZnO has eight sets of optical phonon modes at Γ point of the Brillouin zone, classified as $A_1 + E_1 + 2E_2$ modes (Raman active), $2B_1$ modes (Raman silent), and $A_1 + E_1$ modes (infrared active). Moreover, the A_1 and E_1 modes split into LO and TO components. Figure 3 shows that the Raman spectrum of the ZnONW arrays exhibits only E_2 and A_1 (LO) modes at 438 and 581 cm^{-1}, respectively. The absence of the TO modes could be attributed to the special angle between the wave vector of photons and the c-axial direction of the wurzite ZnO crystals in the near backscattering geometry employed in our measurement. The spectrum was recorded with the incident light exactly perpendicular to the top surface of the ZnONW arrays, namely, the incident light is parallel to the c axis of the
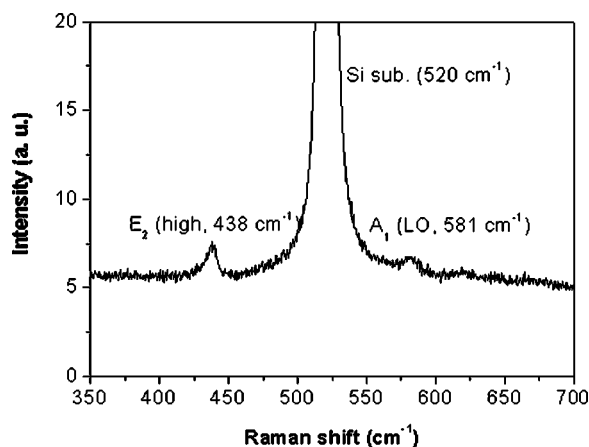
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FIG. 3. Raman spectrum of well-aligned ZnONW arrays on Si substrate.

FIG. 4. PL of ZnONW arrays measured at room temperature.

ZnONWs. In this configuration, only the E_2 and A_1 (LO) modes are allowed, while the A_1 (TO) and E_1 (TO) modes are forbidden according to the Raman selection rules. Thus, the absence of the TO modes in the measurements further confirms that the ZnONWs are highly *c*-axis oriented. Therefore, all of the results inferred from SEM, XRD rocking curves, and Raman data agree with each other.

In order to estimate the magnitude of the stress between the ZnONWs and the Si substrate from the Raman spectra, we use a model based on the result of Frederic Decremps and Julio Pellicer-Porres.[7] They pointed out that the E_2 mode of the wurzite ZnO crystal would shift to a higher frequency under the biaxial compressive stress within the *c*-axis oriented ZnO epilayers by $\Delta\omega$ (cm^{-1})$=4.4\sigma$ (GPa).[7] In our case, the frequency of the E_2 mode observed in the as-synthesized ZnONW arrays is 1 cm^{-1} higher than that observed in the bulk ZnO crystal.[8] The blueshift of the E_2 mode corresponding to the 437 cm^{-1} of the bulk crystal demonstrates that the ZnONWs grown on the Si substrate are under compressive stress, which was estimated to be 0.225 GPa. It has been reported that the biaxial compressive stress within the ZnO films grown on Si (100) was in the range of 0.9 to 9.9 GPa.[9] The smaller stress of the ZnONW arrays compared with that of the ZnO films should be attributed to the stress relaxation effect from the ZnONWs.

Figure 4 shows a representative PL spectrum consisting of a strong UV peak at 3.29 eV (377.0 nm in wavelength) and a weak green band having a broad feature in the range of 2.07 to 2.88 eV (430–600 nm in wavelength). The UV emission band could be related to a near band-edge transition of ZnO, namely, the recombination of free excitons through an exciton–exciton collision process.[10] The green band was generally explained by the radial recombination of a photo-generated hole with the electron in a singly ionized oxygen vacancy.[11] The strong UV emission and the weak green band in the PL spectra indicate that the ZnONWs grown at low temperature have a good crystal quality with few oxygen vacancies.
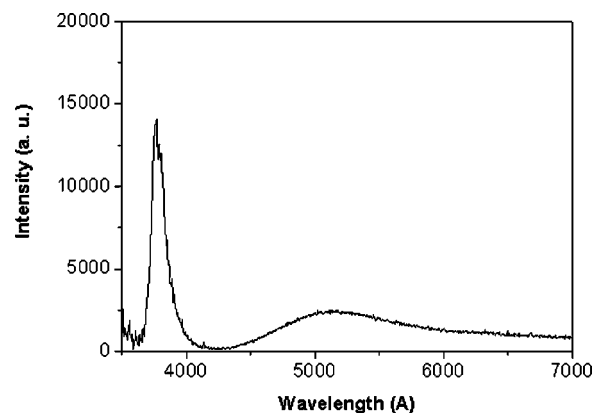
In summary, high-density, vertically oriented ZnONW arrays were fabricated on the Si wafers via a physical vapor deposition method at low growth temperature. SEM observations, XRD, and PL spectra demonstrate that the ZnONW arrays possess a good crystalline character. The nanowires have diameters of 70 to 100 nm and lengths of several micrometers. All of the evidences confirm that the ZnONWs are well aligned and *c*-axis oriented. The low growth temperature of 500 °C is a crucial factor for the production of high-quality ZnONW arrays on Si substrates. The Raman spectra indicate that the ZnONWs on Si are under biaxial compressive stress, estimated to be 0.225 GPa. With the advantage of low-cost, easily controlled deposition spot, potential for scale-up production, and ability to integrate with the Si substrate, this technique has a potential future for fabricating ZnONW array-based optoelectronic devices.

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