Room-temperature, texture-controlled growth of ZnO thin films and their application for growing aligned ZnO nanowire arrays

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Abstract
Texture-controlled growth of ZnO films on substrates of general materials at room temperature by pulsed laser deposition was demonstrated. The texture of the film changed progressively from (001) to (110) to (100) as the laser fluence increased from 2 J cm^{-2} up to 45 J cm^{-2}. Application of the textured films on Si wafers as seed layers for growing aligned ZnO nanowire arrays (grown along the c-axis) with controlled orientation relative to the substrate surface was demonstrated. The individual nanowire forms an epitaxial orientation relationship with the orientation of the grain that nucleated it; therefore the long axis of the nanowire aligns in conformity with the texture of the seed layer.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO is a well-known wide band gap semiconductor and has been studied for many years ([1] for review). Due to its unique electrical and optical properties as well as piezoelectric property, its application has been expanding rapidly in recent years. ZnO also exhibits the most diverse and rich family of nanostructures, ranging from nanowires, nanobelts [2], nanotubes [3], nanorings, nanosprings and nanohelices [4]. As for many technological applications, growth of aligned ZnO nanowire arrays is vitally important for purposes such as field-emission [5], light-emitting diodes, sensor arrays [6], and energy conversion. One of the most noteworthy examples of the nanostructures developed recently is the nanogenerator made of aligned nanowires utilizing the piezoelectricity of ZnO [7].

Growth of aligned nanowires usually requires a single crystal substrate, such as sapphire, which has an epitaxial relationship with ZnO, leading to an aligned growth [8]. For technological applications, however, it is essential to develop a low-temperature growth technique that can grow aligned ZnO nanowire arrays on a general substrate. A possible approach is to develop a textured seed layer of ZnO on the substrate surface, on which the nanowires will be grown. This texture control of the ZnO film is important not only for the application as seed layers but also for the application of the textured film itself in surface acoustic wave (SAW) devices [9]. Therefore, there has been some experimental effort to control the texture of ZnO films by changing the deposition conditions such as bias voltage, ambient pressure, or the application of ion-beam irradiation during the deposition [10, 11, and references therein].

In the present work, we demonstrate a simple, low-temperature, and low-cost technique for controlling the texture of a ZnO thin film on a substrate of general interest. Since the film deposition was achieved at room temperature, the technique can be applied to polymeric substrates as well as inorganic, metallic or oxide substrates. By using these films with controlled texture as a seed layer, aligned nanowire arrays have been grown on the substrate. This work establishes the technological basis for expanding the application of ZnO nanowire arrays for various applications.

2. Experimental details

Our growth is based on pulsed laser deposition (PLD). A ZnO laser ablation target was made by compressing ZnO particles (purchased from Alfa Aesar) and sintering at $\sim$1000 °C to make a disc with a 2.5 cm diameter. The disc was then mounted in the target holder and the chamber was pumped to a vacuum of $\sim$4 × 10^{-7} Torr with a turbomolecular pump. The target was then ablated with KrF UV laser ($\lambda = 248$ nm) in a vacuum of the $\sim$1 × 10^{-6} Torr range. Laser pulse power was varied between 50 and 450 mJ/pulse, and the pulses were shot at a fixed rate of 30 Hz to the target surface. The beam was focused on the target surface with a spot size of 1 × 1 mm, thereby the laser fluence ranged from 5 to 45 J cm^{-2}. All ZnO films were deposited at room temperature on the substrates that were mounted $\sim$4 cm apart from the target for $\sim$20 min or $\sim$36 000 pulses producing e.g. a film of $\sim$700 nm thickness at $\sim$40 J cm^{-2} fluence. Since the deposition is at room temperature, a diverse range of substrates can be used. In the present work, we used silicon wafers, kapton films, and glass plates as substrates to illustrate the universal applicability of the PLD technique. Deposited films were then examined with a PANalytical x-ray diffractometer with Bragg–Brentano parafocusing optics to determine the preferred crystalline orientation of the ZnO film. Texture distribution was examined by measuring the pole figures using a PANalytical X'Pert Pro MRD unit with a parallel Cu Kα x-ray beam (figure 3).

   ZnO nanowires were grown on top of the textured ZnO films on Si substrates employing the well-known vapor–solid–solid (VSS) growth method [13] to test the applicability of textured films for the controlled nanowire growth. The films were mounted in a tube furnace with Zn powder as the source material. The growth system was evacuated to <50 × 10^{-3} Torr, and heated up to 850 °C. Once the reaction temperature of 850 °C was achieved, a mixture of Ar and O$_2$ gas was introduced to the tube furnace in order to grow nanowires on the film. Ar and O$_2$ were introduced at rates of 120 and 8 sccm, respectively. A total pressure of $\sim$50 Torr was maintained throughout the growth of ZnO wires. After 20 min of constant temperature and gas flow, the furnace was cooled to room temperature without gas flow. Grown wires were examined with a FEG SEM (LEO 1550).

3. Results and discussion

In figures 1(a)–(d), XRD patterns of the films deposited at various laser fluencies are plotted. For comparison, a randomly oriented ZnO powder diffraction pattern is shown in figure 1(e). All patterns were taken with θ–2θ scans with the Cu Kα_1 line; the diffracting crystal plane is parallel to the substrate surface. Patterns in figures 1(a) and (b), were taken with $\sim$3° tilt angle in order to avoid strong Si 400 peak (at $2\theta = 69.13°$) from the substrate as shown in figure 1(d). Figure 1(c) was taken with a $\sim$1° tilt. At a laser fluence of 2 J cm^{-2}, the film exhibited strong preference to (001) texture. As the laser fluence to the target increased to $\sim$15 J cm^{-2}, the preferred orientation changed to (110) (see figure 1(c)),
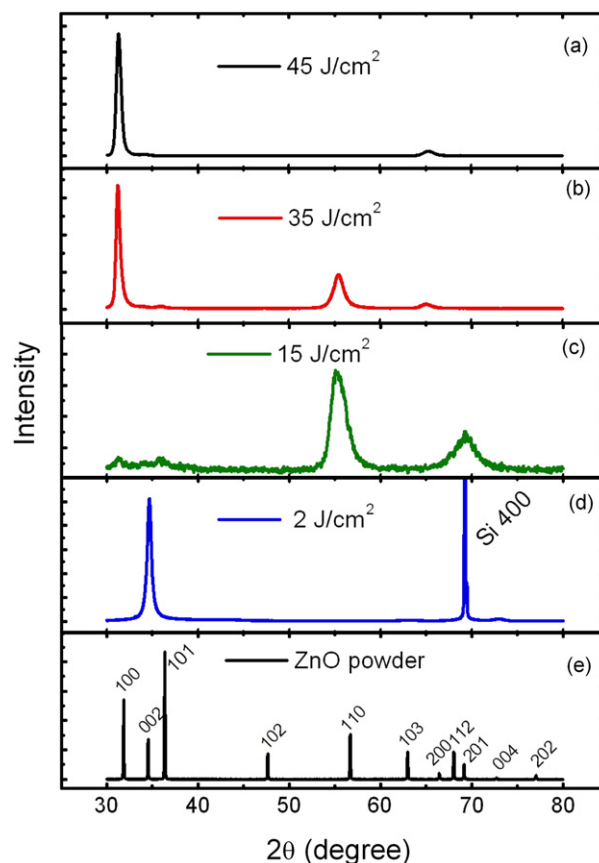

Figure 1. XRD spectra of the ZnO films grown at the laser fluence of (a) 45 J cm^{-2}, (b) 35 J cm^{-2}, (c) 15 J cm^{-2}, (d) 2 J cm^{-2}, and (e) ZnO target made from ZnO powder.

and then eventually to (100) upon with further increase of the laser fluence to $\sim$40 J cm^{-2}. Considering the very different crystalline structure of ZnO and Si, no epitaxial relationship is expected at the interface between the substrate and the film. Therefore, the same trend of texture variation with laser fluence change can be expected for substrates other than Si wafers. As mentioned previously, the deposition procedures were performed at room temperature, which allows the use of polymer substrates as well. Analogous trends were confirmed with kapton and glass substrates. XRD spectra for the ZnO films deposited on kapton and glass substrates are shown in figure 2. The deposition rate on kapton substrate was lower than that on Si wafers. Therefore, the low laser fluence deposition on kapton film resulted in relatively thinner ZnO layers that the broad humps at the lower angle from the polymer substrate was more obvious for the xrd spectrum of this sample. Up to the maximum laser fluence of 45 J cm^{-2}, the texture change from ⟨001⟩ toward ⟨100⟩ is noticeable but not as complete as in the case of ZnO films on Si substrates. It appears that higher laser fluence power is necessary to change the texture of ZnO film from (001) to (100) completely on the glass and kapton substrates than on the Si substrates. But, the general trend of (001) peak suppression as the laser fluence increases is obvious. Due to the incomplete texture change, a peak at 2θ of just below 65°, which is the 103 peak (figure 1(e)), is present for the film on the glass substrate. The presence of 200
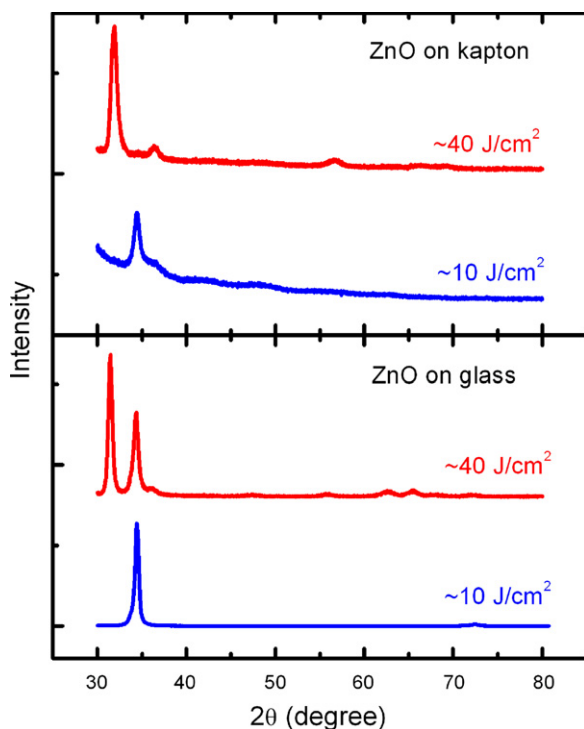
Figure 2. XRD spectra of ZnO films grown on kapton and glass substrates at high (40 J cm^{-2}) and low (10 J cm^{-2}) laser fluencies.

peak at $2\theta = \sim 66°$ in addition to 100 peak supports the strong texture of 100. This 200 peak is also observed in the film on Si substrates (figure 1(a)) but (103) peak is missing because the texture change was complete on Si substrates.

It is noted that all of the peaks measured with as-deposited films (as in figure 1) are broader than the peaks from the powder diffraction pattern of commercial powder (in figure 1(e)) and the peak positions are slightly shifted to lower 2θ angles, meaning a larger lattice spacing or increased vacancy densities. A Williamson–Hall analysis indicated the crystallite sizes to be in the range of a few hundred nm with a 1% strain. Therefore, the crystal structures of the films are less perfect with greater residual stress. Upon post annealing of the film in air at a few hundred °C, the peak width reduced and the peaks moved to the nominal positions for ZnO without changing the original texture. The degree of texture could be measured from the pole figures shown in figures 3(a)–(d). The (001) pole figure shows one strong peak along the direction normal to the substrate plane (figure 3(a)) and the width of the peak is $\sim 14°$, meaning that c-axis of most of the grains in the film are aligned within $\pm 7°$ from the film surface normal. Although the c-axis is aligned, the a-axis is distributed randomly in the film surface as shown in the ring pattern of (101) pole figures (figure 3(b)). Figures 3(c) and (d) are [100] and [101] pole figures from the (100) textured film. The (100) texture results in the peak in the center of figure 3(c) and the weaker ring pattern at $\psi = \sim 60°$ is from the symmetrically equivalent $\langle 110 \rangle$ direction in the hexagonal crystal structure. The FWHM of the (100) pole was measured to be $\sim 9°$, which is smaller than the width of the 001 pole. The two ring patterns in figure 3(d) represent $\langle 101 \rangle$ and $\langle 111 \rangle$, that are also equivalent. They are randomly distributed within the film plane, resulting in ring shapes in the pole figure.

The preferred orientation is thought to be determined from the balance between the energy of the incident atoms from the
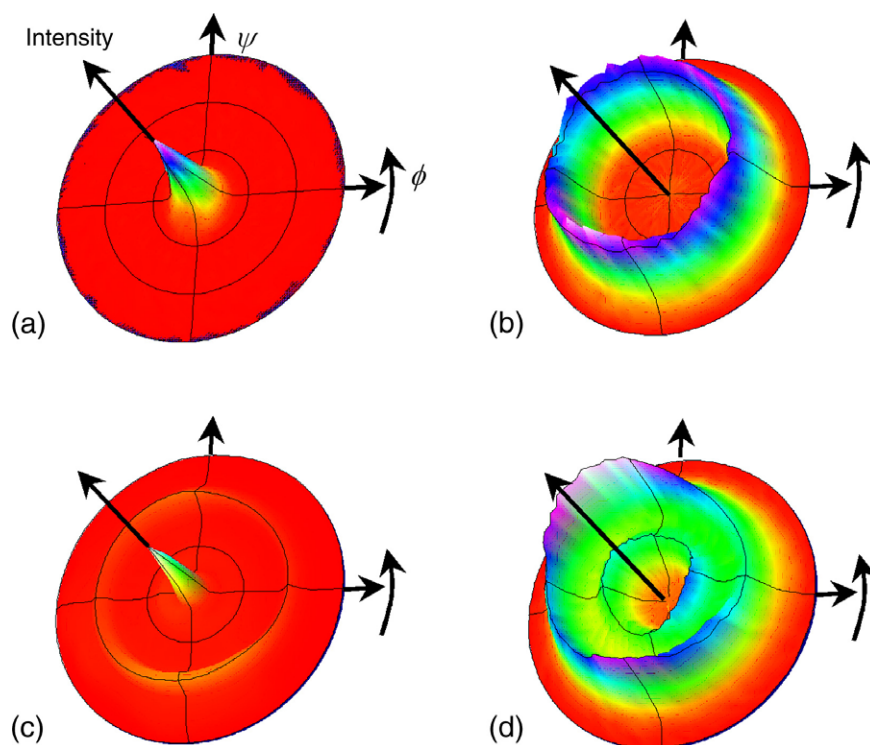

Figure 3. Pole figures of (a) [001], (b) [101] poles of the (001) textured film, and (c) [100], (d) [101] poles of the (100) textured film.
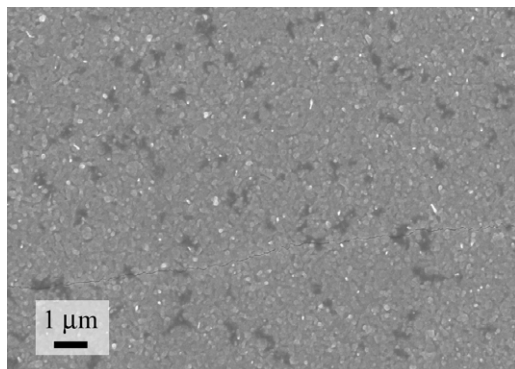
Figure 4. Surface morphology of the ZnO film on Si substrate.

target and the surface energy of the film surface. It is noted that the order of texture change, (001) to (110) to (100), as the laser fluence increases is the same as the order of the atomic planes with increasing surface energy [12]. Under a normal circumstance, the atoms from the target try to form a surface with lowest surface energy and it is natural for ZnO film to grow with (001) texture. As the energy of the atoms increases with higher laser fluence, the atoms with high energy have greater mobility resulting in enhanced surface diffusion of the atoms. When the diffusion of the atoms are limited within the grains, films grow with the texture with higher surface energy, which is (100) for ZnO [10]. When the films were deposited at an elevated substrate temperature, however, the atoms from the target gain more thermal energy after they reach the heated substrate and they take more time migrating on the surface before they settle at the energetically most stable sites, that enables the film to form a texture with the lowest surface energy, (001) texture, as well as more perfect crystalline structure resulting in sharper XRD peaks even at high laser fluence of $\sim$40 J cm^{-2}.

We then used the grown textured films as seed layers for growing ZnO nanowires using the vapor–solid–solid process [13]. The films were mounted in a tube furnace with Zn powder as the source material and ZnO nanowires were grown on top of the ZnO films. Typical morphology of the films before the growth of NWs is shown in figure 4. Although the surface appears optically flat with shiny surface, SEM micrographs reveal very rough surface of the films which is expected to be beneficial to the growth of nanowires with rough edges acting as nucleation sites. Two films with (001) and (100) textures, respectively, were positioned side by side at the same distance from the source material in order to ensure identical ZnO nanowire growth conditions on both samples. The morphology of the wires was examined with a FEG scanning electron microscopy (SEM). Figures 5(a) and (b) show the ZnO nanowires grown on the film with (001) texture, and figures 5(c) and (d) are ZnO nanowires grown on the film with (100) texture. All wires grew with the [001] direction along the length of the wire, and are in epitaxy with the textured thin film layer at the base. Therefore, all the wires on the ZnO film with (001) texture grew perpendicular to the surface of the film, and the wires on the film with (100) texture grew in the plane of the substrate. Within a grain of a few μm in width (figure 5(c)), all wires grew in the same direction (*c*-axis direction of the grain), but the growth direction varied among grains within the film surface.

4. Conclusions

In summary, we have shown that the control of ZnO film texture can be achieved at room temperature via the control of the energy of the deposited atoms. The structure of the deposited film is irrelevant to the substrate that various materials could be used as substrates for the film. ZnO nanowires can be grown on top of these textured films and they grew in epitaxy with the films as shown with the films
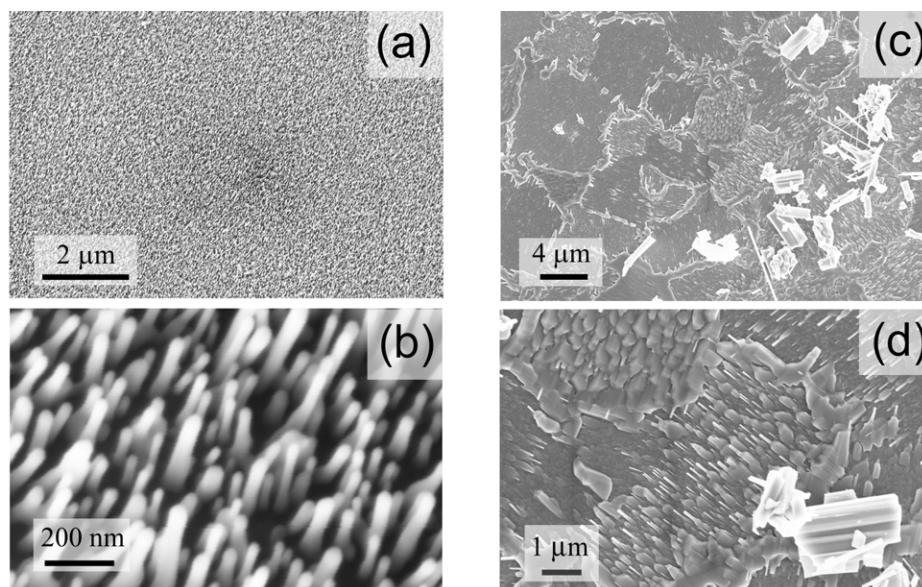

Figure 5. SEM micrographs at various magnifications of ZnO nanowires grown on (001) textured film ((a) and (b)), and (100) textured film ((c) and (d)) at various magnifications. Micrographs in (a) and (b) were taken with specimen tilted by 30° to observe the nanowires grown perpendicular to the specimen surface, and those in (b) were taken looking directly down from the direction normal to the sample surface.

on Si wafer. For the textured films on the substrates with lower melting points, other methods for nanowire growth [14] can be applied to grow wires on top of seed layers. Therefore, the use of these textured films enables the growth of nanowires with controlled degree of nanowire alignment.

Acknowledgments

References

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