Growth Control of ZnO Nano-Crystals by Multi-Beam Interference Patterning

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We have succeeded in controlling growth density of the ZnO nanowires by introduction of a ZnO buffer layer. Low-density hexagonal cone-shape ZnO cores are formed on the buffer layer, and vertically-aligned ZnO nanowires are grown on the cores. The density of the nanowires was decreased by laser irradiation to the buffer layer before growth of the ZnO nanowires. In addition, periodic growth of ZnO nano-crystals was demonstrated using four beam interference patterning.

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1. Introduction

One-dimensional (1D) nanomaterials have received increasing attention due to their unique properties. Among these materials, zinc oxide (ZnO) nano-crystal is great interest for optoelectronic applications in particular ultraviolet (UV) region such as UV-LEDs [1,2], UV-lasers [3], and UV-photosensors [4], due to the unique electronic and optoelectronic properties, which is wide band gap (3.37 eV) and large exciton binding energy (60 meV).

For the practical optoelectronic applications based on the ZnO nano-crystals, however, fabrication of layered structures for *p-n* junction and control of nanowire growth direction, shape, density, and position are essentially required. As regards control of shape, in our study, we have succeeded in growing various ZnO nano-crystrals, such as nanowires, nanowalls, and nanorods, by nanoparticle-assisted pulsed laser deposition (NAPLD) with changing growth conditions. Concerning the growth direction of the ZnO nano-crystals, vertically- and horizontally-aligned ZnO nanowires have been achieved by using a pre-annealed sapphire substrate [5,6]. A control of the density have been achieved by varying the repetition rate and laser fluence of the ablation laser [7]. In addition, we found that preparation of a ZnO buffer layer before growth of the nanowires affects the density and the alignment of the nanowires. However, control of position has not yet been realized in NAPLD. In order to make patterned-structures, a lithographic or imprinting technique is generally used [8-10]. Unfortunately, however, they need complex procedures and a catalyst. In this study, a simple method of laser irradiation to the buffer layer was introduced to control the growth position of ZnO nano-crystals. The density of the nanowire grown on laser-irradiated buffer layer clearly decreased. Thus, more active control of not only the density but the growth position is expected by introduction of the laser irradiation to buffer layer without complex procedures and catalysts. In the experiment, interference laser irradiation was adopted for patterned growth of the ZnO nano-crystals.

2. Experiment

In this experiment, a sintered source target of ZnO was used in synthesizing ZnO nano-crystals. An *a*-plane sapphire substrate (10 mm×10 mm×0.5 mm) was put on a SiC heater in a vacuum chamber and the target-substrate distance was set to be 40 mm. The ZnO target was ablated with the third harmonics of a Q-switched Nd:YAG laser at 355 nm with a repetition rate of 10 Hz and a fluence of about 1 J/cm^2. The irradiated spot size was about 2 mm in a diameter. A ZnO buffer layer was deposited on the sapphire substrate at a background oxygen pressure of 3.3 Pa with a substrate temperature of 650 ºC for 2 minutes. The thickness of the buffer layer was about 100 nm. After deposition the buffer layer, the sample was taken out from the chamber and irradiated by a single Nd:YAG laser pulse of 355 nm. Subsequently, the irradiated sample was placed in the chamber again, and then ZnO nano-crystals were grown on the buffer layer at background argon gas of 27 kPa and a laser fluence of 0.5 J/cm^2 with a substrate temperature of 750 ºC for 20 minutes (12000 pulses).

3. Results and discussions

3.1 Laser irradiation to ZnO buffer layer

Fig. 1 shows the atomic force microscopy (AEM) images of ZnO buffer layers of as-grown and the laser-

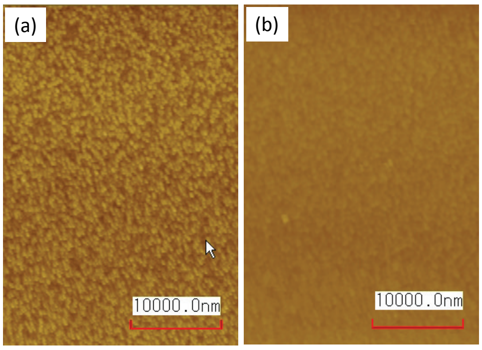

Fig. 1 AFM images of ZnO buffer layer, (a)as-grown surface and (b) laser-irradiated surface.

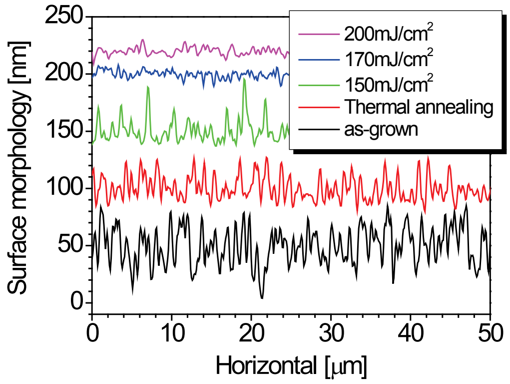

Fig. 2 Surface profile of the ZnObuffer layer.

Table 1 Surface roughness of the ZnO buffer layer.

	as-grown	Thermal annealed	Laser-irradiated		
			150 mJ/cm^2	170 mJ/cm^2	200 mJ/cm^2
RMS	17.3nm	13.3nm	13.4nm	4.3nm	3.8nm

irradiated surface with a laser fluence of 200 mJ/cm^2. The as-grown layer surface consists of small grains. The grain size was 200-300 nm and the surface roughness rms approximates 17.3 nm. On the other hand, the laser-irradiated layer has a smooth surface. Fig. 2 and Table 1 show the surface profile and surface roughness rms of the buffer layers, respectively. The surface roughness of the buffer layer clearly decreased to 13.4–3.8 nm by laser irradiation around 150-200mJ/cm^2. In most cases, a laser-irradiated surface will be more rough by surface texturization [11,12]. In our case, the roughness was improved with increasing the laser fluence in the low energy range, which is below the laser ablation threshold. It is considered that the ZnO grains are connected with each other by rapid laser annealing. A similar observation of the surface smoothing has been reported for a KrF excimer laser irradiation [13]. The roughness hardly changed by thermal annealing. For as-grown and the laser-irradiated buffer layers, only (002) and (004) peaks were obtained in the X-ray diffraction (XRD) measurement, which indicates that the layers are *c*-oriented.

3.2 Growth of ZnO nano-crystals on laser-irradiated ZnO buffer layer

Fig. 3(a) shows the SEM image of ZnO nanowires synthesized on the buffer layer. As mentioned in the experiment, the ZnO nanowires were grown at background argon gas of 27 kPa for 12000 pulses. Almost nanowires are vertically well-aligned and grown on hexagonal cone-shape ZnO cores. In the XRD, (002) and (004) peaks were detected from them (result not shown here), indicating the nanowires had high crystalline quality and preferential orientation along the c-axis. The lengths and diameters of the nanowires were 1 μm and 100 nm, respectively. More dense nanowires are grown when no buffer layer is introduced. Although the growth mechanism of ZnO nanowires on sapphire is still under investigation, the crystal polarity has a crucial role in both the nucleation and the growth of nanowires [14], because wurtzite ZnO has polar surfaces of

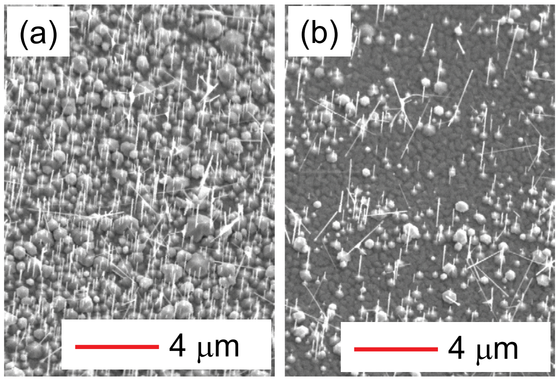

Fig. 3 SEM images of ZnO nanowires on (a) the buffer layer and (b) the laser-irradiated buffer layer.

positively charged Zn-(0001) and negatively charged O-$(000\bar{1})$. Y. Sun's group reported that an initial ZnO layer grown on sapphire under the ZnO nanostructure growth condition contains high-density threading dislocations (TD) [15], and Zn-polar nanorods (oriented in the +*c* direction) grew on O-polar under-layer (oriented in the –*c* direction) [16]. In our experiment, it is considered that the prepared ZnO buffer film consists of relatively low density TDs compared with the initial ZnO layer on sapphire, and prevent nanowire nucleation since the incoming ZnO incorporates much more effectively into the ZnO buffer layer. Similar result was reported by B. Q. Cao *et al* [17]. Fig. 3(b) shows the ZnO nanowires grown on the laser irradiated buffer layer. The fluence of the laser pulse was estimated to be 120 mJ/cm^2. The nanowire density clearly decreased due to laser irradiation to the buffer layer. Thus, the laser irradiation may decrease not only the surface roughness of the buffer layer, but also the TD density by connecting the grains each other. Although the growth mechanism of the nanowire on the laser-irradiated ZnO buffer layer by NAPLD have been under investigation, ZnO nanowire density can be controlled by laser irradiation. In addition, it is expected to control the growth position of the ZnO nanocrystals by selective irradiation, such as interfering laser irradiation. In this study, four-beam interference irradiation [18,19] was utilized as shown in Fig.4.

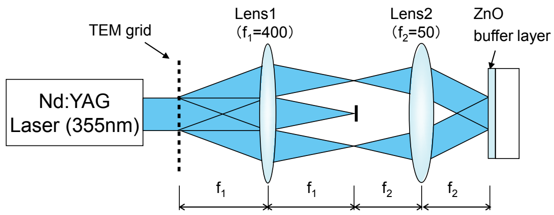

Fig. 4 Schematic of 4-beam laser interference irradiation.

3.3 Introduction of laser interference irradiation

A TEM grid (400 mesh) was used as a transmission beam splitter. A flat-top beam with a diameter of about 2 mm was irradiated to the beam splitter. The beam was split into several diffracted beams and collimated by the lens 1. Only four beams were selected by a spatial filter and then illuminated on the same spot through the lens 2. By configuring a demagnification system, the spot diameter

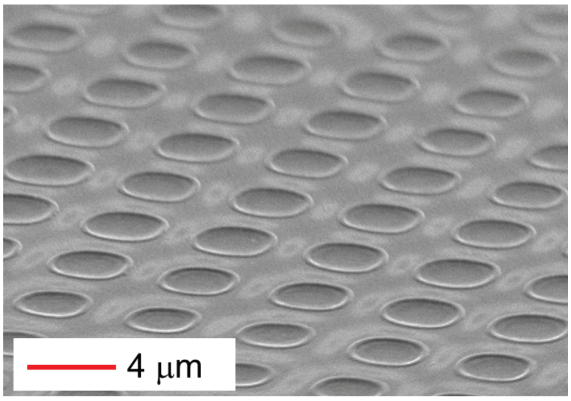

Fig. 5 SEM image of the buffer layer irradiated with the interfering laser beams.

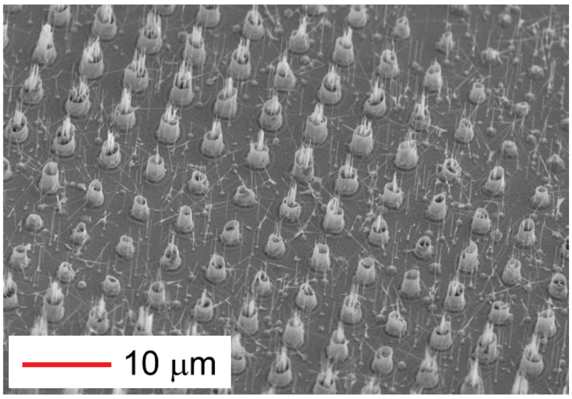

Fig. 6 SEM image of the ZnO nano-crystals grown on the buffer layer irradiated with the interfering laser beams.

was reduced to $(f_2/f_1)\cdot 2$ mm. An interference pattern is formed at the illuminated spot on the buffer layer. A pitch of the four-beam interference pattern can be calculated by $(f_2/f_1)\cdot d_1/\sqrt{2}$, where d_1 is the period of the transmission beam splitter. In the experiment, d_1 was 63.5 µm (1 inch/400 mesh), and the focal lengths of lens 1 and lens 2 were 400 mm and 50 mm, respectively. Thus, the pitch of the interference pattern was calculated to be 5.6 µm, and a spot size of each bright pattern was estimated to be 4.3 µm at $1/e^2$ intensity. After a single shot interference irradiation, the periodic pattern was formed on the buffer layer, as shown in Fig.5. In this case, the buffer layer was ablated at a center of the irradiated spot, and ablation craters were formed due to the high laser fluence of about 1 J/cm^2. The pattern period of the periodic structure showed a good agreement with the numerical estimation. As the crater size depends on the laser fluence, the size of those craters was around 2.5µm in this case. After interference laser irradiation to the buffer layer, ZnO nano-crystals were subsequently grown on the layer. Fig.6 shows the SEM images of the nano-crystals grown on the buffer layer irradiated with the interfering laser beams. Periodic structures are formed on the laser-irradiated buffer layer. ZnO nanowalls are synthesized from the edge of each irradiation spot. Only two characteristic peaks of (0002) and (0004) from the ZnO hexagonal wurtzite structure were observed from the structure in the XRD measurement. The ZnO nanowalls were preferentially grown along the circumferences of those craters. Since growth rate along the +*c* direction is higher than along the -*c* direction [14], surface polarity at the edge of the crater might be changed by laser ablation. Although we need to investigate the growth mechanism and a relation between the laser fluence and the structure of the ZnO nano-crystals, interference laser irradiation can be used as one of the effective technique to control the growth position and morphology of the ZnO nano-crystals synthesized by NAPLD.

4. Conclusions

We have demonstrated the periodic growth of the ZnO nano-crystals by introduction of a ZnO buffer layer and interference laser irradiation. ZnO nanowire density was decreased by laser irradiation to the ZnO buffer layer. We considered that the laser irradiation may decrease not only the surface roughness of the buffer layer, but also the TD density by connecting the grains each other. Four-beam laser interference was utilized to form the periodic pattern with a single laser shot. Interference laser irradiation to the buffer layer can be used as one of the effective technique to control the growth position and morphology of the ZnO nano-crystals synthesized by NAPLD.

Acknowledgments and Appendixes

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