Characterization of Zinc Oxide Micropatterns Deposited on Self-Assembled Monolayer Template

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自己組織膜テンプレート上に析出した酸化亜鉛マイクロパターンのキャラクタリゼーション

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ZnO micropatterns were fabricated through site-selective electroless deposition using self-assembled monolayer template terminated with phenyl/OH-surface functional groups. ZnO was deposited only on the Pd-catalyzed phenyl-regions of the substrate. The feature edge acuity of the ZnO patterns was estimated as several times of the particle size of $\sim 0.2 \mu\text{m}$. ZnO single crystal particles were grown on the substrate forming a dense, mono-particulate layer. The broadening of X-ray diffraction peaks was attributed to the strain due to the defects originated in an aqueous solution. Transmission electron micrographs revealed that ZnO particles were continuously grown on the catalyzed substrate.

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1. Introduction

Zinc oxide is one of the representative electro ceramic materials and it has good properties for varistors, transparent electrodes, and surface acoustic wave devices. Especially, it has been a promising phosphor material for high-resolution field emission displays, because of its ability to retain high efficiency even at low voltage excitation.¹⁾ Patterning techniques are useful for arrangement of phosphor or wiring electrodes. For integration technology of ceramic materials, micropatterns are greatly expected in various applications.

Conventionally, patterned ceramic thin films are formed by selective etching or liftoff processes using photoresists. However, it has been hard to find suitable etching conditions free of influence on the substrate, or to obtain high-resolution pattern edges even after tearing the ceramic films in liftoff processes. To solve these problems, techniques of site-selective growth have recently been developed. Huang et al. have reported a novel synthesis of ZnO nanowires through a vapor-liquid-solid (VLS) process on Au-catalyzed surfaces.^{2),3)} Photo-enhanced chemical vapor deposition method⁴⁾ is another example. Since these growth processes require heat-treatments at high-temperatures, which can damage substances already present on the substrates, a new micropatterning technique available at room temperature is desired.

For such demands, there has been a growing interest in the so-called 'biomimetic' approach to site-selective deposition to prepare ceramic oxide patterns at low temperatures in solutions, using self-assembled monolayer (SAM) templates.^{5)–11)} By modifying the surface functional groups of the substrates with SAMs, the interactions with inorganic substances can be controlled and the deposition manner can be designed. So far, the authors attempted patterning ZnO on SAMs through electroless deposition of ZnF(OH).^{10),11)} The precipitate particles, however, were not small enough for high-resolution patterning.

Recently, the present authors have succeeded in low-temperature fabrication of 1- μm width ZnO line patterns using a phenyl/OH-terminated patterned SAM as a template and demonstrated cathodoluminescence of visible light from the

ZnO patterns.¹²⁾ Catalyst of Pd/Sn colloid was adhered to the phenyl-surfaces, as performed for the selective electroless plating of Cu or Ni proposed by Calvert et al.^{13),14)} ZnO was grown on the catalyzed phenyl-surfaces by the electroless deposition method developed by Izaki.^{15),16)} In order to improve the pattern resolution and the film properties, it is necessary to understand and control the deposition process more precisely. In the present paper, we have investigated the microstructure of the ZnO film deposited on the catalyzed SAM mainly by using transmission electron microscopes (TEM), to clarify the mechanism of film growth.

2. Experimental procedure

Figure 1 outlines our strategy for selective-deposition scheme employed to fabricate ZnO patterns. A SAM of phenyltrichlorosilane (PTCS) was prepared on a cleaned Si single crystal substrate ($\langle 100 \rangle$, p-type, $15 \times 15 \times 0.5 \text{ mm}$). The substrate was cleaned by soaking in 1:1 v/v HCl/CH₃OH for 30 min, and then in concentrated H₂SO₄ for 30 min. The substrate was immersed in an anhydrous toluene solution containing 1 vol% PTCS for 5 min under a N₂ atmosphere, followed by baking at 120°C for 5 min in air. The resultant SAM was exposed to UV light through a photo-mask for 2 h in order to pattern the surface with OH- and phenyl-groups.¹⁴⁾

Prior to the deposition of ZnO, the phenyl-group regions of the substrate were catalyzed by Pd colloid particles. The substrate was immersed in the solution of Pd/Sn colloid (Cataposit 44, SHIPLEY), which contained $1.8 \times 10^{-3} \text{ M}$ PdCl₂ and $4.2 \times 10^{-2} \text{ M}$ SnCl₂, at 45°C for 3 min. Then, the substrate was soaked in an acidic solution of HBF₄ (Accelerator 19, SHIPLEY) at room temperature for 5 min for acceleration. For electroless deposition of ZnO, the SAM substrate was immersed in an aqueous solution of Zn(NO₃)₂ (0.05 M) and dimethylamine-borane (DMAB) (0.01 M) at 55°C for 30 min.

The following characterization was carried out for both ZnO samples deposited on the UV-patterned and non-patterned PTCS SAM substrates. The material deposited on the substrate was identified by X-ray diffraction (XRD;

Fig. 1. Schematic diagram of site-selective electroless deposition of ZnO on the phenyltrichlorosilane (PTCS) self-assembled monolayer (SAM) template. (a) Preparation of PTCS SAM. (b) Patterning of the SAM by exposing UV light through a photomask. (c) Site-selective catalyzation of the phenyl-surfaces and ZnO deposition on the catalyst.

Rint2000, Rigaku) measurement using Cu K α radiation. The crystallite size was estimated from the broadening of XRD peaks using LaB6 (SRM-660a, NIST) as the standard. Microstructures of the ZnO film were observed using scanning electron microscopes (SEM; JSM-6400, JEOL and S-5000, Hitachi), an atomic force microscope (AFM; Nanoscope IIIa, Digital Instruments) with contact mode and TEMs (JEM-2000EX and JEM-4000EX, JEOL). The excitation voltages for TEM were 200 and 400 kV for low- and high-resolution images, respectively. For the TEM observation, a foil was prepared by cutting the sample coated with epoxy resin. The elements of the deposits on the substrate were determined by energy-dispersive X-ray analysis (EDX) equipped in the TEM.

3. Results and discussion

A typical SEM photograph of ZnO micropattern obtained by the present process is shown in Fig. 2(a). The white regions correspond to ZnO, which indicate excellent site-selectivity of deposition occurring only on the phenyl-regions. The SEM image of the edge of the pattern is shown in Fig. 2(b). The feature edge roughness was estimated as several times of the particle size which is about 0.2 μm .

The XRD pattern of the as-deposited film on the UV-patterned SAM substrate is illustrated in Fig. 3(a). A similar pattern was obtained for the sample deposited on the non-patterned substrate. The material deposited on the substrate was confirmed as polycrystalline ZnO, which did not show significant preferred orientation, though the (0002) peak was sharper than other diffraction peaks.

Izaki described the chemical reactions of the ZnO electroless deposition process as the following scheme;¹⁵⁾

By the electrons produced through oxidation of DMAB (Eq. (2)), reduction of NO_3^- ion into NO_2^- ion proceeds (Eq. (3)), and then ZnO is deposited according to an increase in

Fig. 2. SEM photographs of (a) 8 μm -width ZnO lines and (b) the edge of the pattern.

pH. The above reactions are greatly promoted by Pd catalyst. When using a Pd-catalyzed substrate, ZnO can be grown only on the substrate in high yield under the solution

Fig. 3. X-ray diffraction pattern of (a) ZnO polycrystalline film deposited on the catalyzed substrate with (b) the JCPDS Card data (No. 36-1451) for comparison.

conditions where spontaneous precipitation cannot occur. Probably because the catalyst colloid was dispersed randomly on the substrate, ZnO grew with random orientation. Izaki reported the preparation of a highly oriented ZnO particulate film on a single crystalline alumina substrate when using UV light instead of Pd colloid catalyst for initiating ZnO deposition.¹⁷⁾

The experimental fact that ZnO was deposited only on the phenyl-surfaces but not on the UV-irradiated OH-surfaces indicates that the Pd/Sn catalyst particles adhered only to the phenyl-surfaces. The combination of the phenyl-surface and the UV-irradiated OH-surfaces lead to one of the best results of site-selectivity for ZnO deposition, when we examined various SAMs terminated with amino, hydrocarbon, pyridine, or sulfonyl surface functional groups.¹⁸⁾ The amount of Pd adhered to the SAM substrate was so small that it was not detected by EDX equipped in the SEM. Further discussion will be made later based on TEM observations.

The AFM image of the ZnO surface shown in Fig. 4(a) indicates that the particle size was relatively uniform and the average diameter was about $0.2 \mu\text{m}$. The substrate was almost fully covered with the particles, although some voids were still present. The standard deviation of the surface roughness (rms) was estimated from the cross sectional view (Fig. 4(b)) to be about 30 nm, which means that the surface was flat in the scale of the particle size.

A typical cross-sectional SEM photograph of ZnO deposited on the catalyzed phenyl-terminated substrate is shown in Fig. 5. The particles look well connected to the substrate and to the neighbor ZnO particles. The ZnO film was proved to be composed of an almost mono-particulate layer, few particles being observed on it. It is different from the texture of usual polycrystalline films composed of multilayers of particles. When a scotch tape test was applied to the ZnO film, ZnO remained on the substrate, suggesting that the ZnO particles adhered to the substrate relatively strongly.

In order to see the relationship among the substrate, catalyst colloid and ZnO particles, the cross-section was observed by TEM. Figures 6(a) and (b) show cross-sectional images of low- and high-resolution, respectively. Fig. 6(a) was a scanning (STEM) image. ZnO particles of about $0.1 \mu\text{m}$ in diameter were deposited well connected with each

Fig. 4. (a) AFM image of the surface of ZnO deposited on the catalyzed substrate. (b) The cross section view along the line indicated in (a).

Fig. 5. Cross-sectional SEM photograph of ZnO deposited on the catalyzed substrate.

other. Crystalline ZnO grew continuously on the silicon substrate with a $\sim 6 \text{ nm}$ -thick intermediate amorphous layer composed of native SiO_2 and SAM. Small crystalline catalyst particles of about 3 nm in diameter showing the lattice fringes were observed to be buried in the SiO_2 amorphous layer at the interface between ZnO and the amorphous layer. The Pd colloid particles were not so densely dispersed to fully cover the substrate. Interfaces with few catalyst particles were also observed.

The results of TEM-EDX analysis for the regions in a ZnO particle and around catalyst particles are shown in Fig. 7. For ZnO particles, signals of only Zn and O were detected. Additional detection of Pd and Sn in the region around the small particles at the interface was confirmed. Smaller intensity of Sn than that of Pd means that almost Sn in the original Pd/Sn colloid (the content of Sn was about 20 times that of Pd) was removed by acceleration treatment in

Fig. 6. (a) Low- and (b) high-resolution cross-sectional TEM images of the ZnO particulate film deposited on the catalyzed substrate. ((a) scanning image.)

the acid solution. Surrounding layer of $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ may have been dissolved but Sn in the Pd-Sn alloy cores remained. Most of carbon came from the epoxy polymer used for coating the substrate. Although the extra peak at 4.5 keV corresponds to Ti, we did not detect it by TOF-SIMS.

Selected-area electron diffraction patterns were taken for three ZnO particles. The crystal orientation in each particle was random. Clear diffraction spots reveal that each ZnO particle is a single crystal. Figure 8 exemplifies a typical result.

From the broadening of the XRD peaks, we estimated the crystallite sizes parallel and vertical to the c -axis to be 110 nm and 40 nm, respectively. However, the estimation was not consistent with the present TEM results that the ZnO particles were single crystals. Accordingly, the broadening of the XRD peaks should be attributed to the strain to the direction vertical to the c -axis.¹⁹⁾ The strain is probably due to the defects originated during the growth in an aqueous solution.

The ZnO particles deposited on the catalyzed substrate were almost equigranular single crystals much larger than the catalyst particles (2–3 orders difference). There are two possible growth models to explain the above experimental results. One is the selective nucleation of ZnO occurring on only some but not all of the catalyst particles, followed by successive growth. The other is that nucleation took place on all the catalyst particles and some particles grew by consuming of the other small particles. In the present study, there were not significantly small particles remaining at in-

Fig. 7. EDX analysis results for the regions (a) in a ZnO particle and (b) around catalyst particles.

terfaces between the substrate and ZnO, which is often observed in the case of epitaxial thin film growth through gas-phase processes.²⁰⁾ By dissolution-deposition process in aqueous solutions, it would be possible for small particles to disappear. In order to clarify the growth mechanism, it is necessary to investigate the early stage of growth.

4. Conclusions

In the present study, ZnO micropatterns were synthesized through site-selective deposition only on the Pd-catalyzed phenyl-surfaces of the photo-patterned PTCS SAM. By means of SEM, XRD, AFM and TEM, the ZnO deposits were characterized. The results can be summarized as follows;

- (1) The feature edge acuity of the ZnO micropatterns was estimated as several times of the particle size $\sim 0.2 \mu\text{m}$.
- (2) ZnO single crystal particles $\sim 0.2 \mu\text{m}$ were grown on the substrate forming a dense, mono-particulate layer.
- (3) The reason for the broadening of the XRD peaks was regarded as strain due to defects originated in an aqueous solution.
- (4) TEM observation revealed that ZnO particles were

Fig. 8. Selected-area electron diffraction obtained for a ZnO particle. The incident beam was along $[3\bar{3}0]$.

continuously grown on the catalyzed substrate.

(5) Pd/Sn catalyst particles ~ 3 nm were observed at the interface between the substrate and ZnO.

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