Low-Temperature Fabrication of Zinc Oxide Micropatterns Using Selective Electroless Deposition

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Zinc oxide (ZnO) micropatterns were synthesized site-selectively on photocatalytically activated regions of TiO2 in an aqueous solution of zinc nitrate and dimethylamine-borane at 55°C by an electroless deposition process. The as-deposited ZnO micropatterns showed a polycrystalline wurtzite structure with a thickness of approximately 0.1 μm. The ZnO micropatterns emitted ultraviolet light at 380 nm due to the recombination of bound excitons and broad visible-light luminescence (500-800 nm).

Since the first report of ultraviolet by laser from zinc oxide (ZnO),1,2 substantial effort has been devoted to the development of synthetic methodologies for ZnO films. Among the various techniques described in the literature, evaporation and condensation processes are favored for their simplicity and high-quality products, but these gas-phase approaches generally require economically prohibitive temperatures of 800-900°C.3,4 Despite recent metallicorganic chemical vapor deposition (MOCVD) schemes that reduced the deposition temperature to 450°C by using organo metallic zinc precursors,5 the commercial potential of gas-phase grown ZnO films remains constrained by the size and cost of the vapor deposition systems. Thus, a low-temperature, large-scale, and versatile synthetic process is needed before ZnO can have realistic applications in solar energy conversion,6 light emission,7 and other promising synthetic processes.8-10

Solution approaches to ZnO films are appealing because of their low growth temperatures and good potential for scale-up. Because of this, Izaki et al. developed an electroless deposition (ELD) method for polycrystalline particulate ZnO films that is based on the reduction of nitrate ions and that uses dimethylamine borane (DMAB).11,12 By immersing substrates in an aqueous solution maintained at ~60°C, crystalline ZnO particulate films were obtained on the Pd catalyst particles attached to the substrates. However, in spite of the importance of the solution approaches to the fabrication of ZnO films, the chemical deposition mechanism of the ZnO film from aqueous solution is controversial, and several mechanisms have been proposed. Izaki et al. explained that the reduction reaction of the nitrate ion plays an important role in ZnO formation from the solution and is driven by the oxidation reaction of DMAB contained in the solution.1,12 It was also proposed that the deposition mechanism of the ZnO film originates from precipitation of Zn(OH)2 by the reduction of oxygen,13,14 and participation of superoxide radicals by the reduction of oxygen.15

Selective ELD has recently become very promising for micro-/nanostructuring a wide range of materials; that is, a method in which metal is electrolessly plated up from a predetermined pattern. In particular, it is proving increasingly useful in semiconductor and packaging technologies. A major requirement prior to performing selective ELD is the catalytic Pd seed (the placement and activation of the seed on the surface) and its selectivity: the seed must be confined to specified regions of the substrate and be completely absent from other regions. This can have been achieved either by selective deactivation of a catalytically active substrate or by the selective activation of a nonreactive surface. Several approaches that seek to create catalytically active Pd patterns with high activity and contrast have been explored. They include photopatterning of pretreated substrates combined with the deposition of metal films,16,17 selective modification of catalyst-binding monolayers,18,21 and microcontact printing of a catalyst onto substrates.22,23

Recently, we have succeeded in the controlled deposition of Pd metal nanoparticles using photocatalytically active properties of photocatalysts such as TiO2 or SnO2.24 Results have shown that the Pd nanoparticles were selectively adhered to regions having specific surface properties, such as the photocatalytically activated surface on the photocatalysts. Using the Pd as a catalytic seed for the ELD in the present study, we describe a simple but powerful way to fabricate homogeneously and patterned films of ZnO under mild aqueous conditions via selective ELD. As a result, ZnO micropatterns with a resolution of ~5 μm in width were successfully deposited electrolessly along the Pd catalyst attached to the photocatalytically activated surfaces.

Figure 1 schematically outlines the selective ELD process used for the patterned growth of ZnO on glass substrates. The glass substrates were cleaned for 10 min by immersion in a Piranha solution [a 7:3 (v/v) mixture of 98% H2SO4 and 30% H2O2], followed by rinsing in deionized water and drying on a 120°C hot plate. Caution: the piranha solution reacts violently with most organic materials and must be handled with extreme care. In order to obtain the uniform photocatalytic layer of TiO2 for a large area, n-butyl polytanate (Tyzor BTP, DuPont, 5% in 2-propanol) was deposited on the substrate by spin-coating and was baked at 100°C in air. The as-produced films were transparent, uniform in their thickness of 0.03-0.1 μm, and amorphous, as stated in the DuPont Tyzor brochure. The irradiation of TiO2 photocatalysts with photons having energies greater than the bandgap gives rise to excited-state electrons in the conduction band and holes in the valence band.25 UV-visible spectra of the amorphous TiO2 film used in this work showed that the main absorption edge was situated at ~320 nm, corresponding to an optical bandgap of 3.95 eV, whereas the absorption edge for anatase TiO2 was at ~380 nm (3.2 eV).26 It is reported that the increase in the bandgap energies of TiO2 film may be caused by a change in band structure as a result of small crystallite sizes.27 As a result, irradiation of a UV light with a wavelength of less than 320 nm would generate excited electron/hole pairs, enabling the use of photocatalytic properties.28 Subsequently, the water-soluble polyvinyl alcohol (PVA) layer was made by spin-coating on top of the TiO2 film and drying for several minutes at 100°C. The raw materials used for the PVA layer are PVA (Polyscience, 5%, M: 6000), oxalic acid (0.05 M), and triethanolamine (0.01 M). The thickness of the PVA layer was estimated to 0.04 μm. Here, the PVA layer was used as hole scavengers,29-31 which would suppress the recombination of the excited electrons and holes formed during the photocatalytic reaction of TiO2. Therefore, the hole scavengers prolonged the lifetime of the excited electron, which induced a reduction reaction with metal cations. In this work, we used the broad wavelengths of a 1 kW high-pressure Hg lamp. The irradiance at the sample position was about 10 mW/cm².

After UV irradiation for 1.5 min, the substrates were immersed in an aqueous solution of Pd salt (PdCl2·0.3 GL-1, KCl 10 GL-1, HCl 10 M L-1) for 1.5 min. The photoactivated TiO2 possesses reducing power for Pd ions and Pd metal layer simultaneously de-
posited on the irradiated area by the photocatalytic reaction. However, the reducing power fades away during storage. To see the effect of postexposure time delay, the photoactivated substrate was treated with Ag⁺ ion instead of Pd²⁺ ion. The microscopic images of Ag patterns after various postexposure time delays between UV exposure and Ag⁺ ion treatment are shown in Fig. 2. The reducing capability of the photoactivated TiO₂ remains for up to 12.5 min. Pd patterning is also considered to show a similar tendency. For this reason the Pd²⁺ ion treatment was carried out within 10 min after the UV exposure.

Moreover, a Pd/H₂O₂/H₂O₀ pattern accurately matching the photomask was obtained by light irradiation between 1.5 and 2 min. When the irradiation time was shorter than 1.5 min, however, the Pd/H₂O₂/H₂O₀ pattern was incomplete, because the extent of reduction of Pd(II) on the irradiated area was insufficient. In addition, when the irradiation time was longer than 2 min, the Pd(0) patterns became blurred. In this case, it is likely that the Pd(II) near the photomask is also reduced via the lateral diffusion of electrons excited in the TiO₂ thin film through the already reduced Pd/H₂O₂/H₂O₀ layer.

Figures 3a-d show a scanning electron microscopy (SEM) image and high-resolution transmission electron microscopy (HR-TEM) data of the catalytic Pd seeds that are selectively deposited by the photocatalytic reaction on the amorphous TiO₂ films. SEM images were obtained using a Hitachi S4700 instrument with a tungsten single-crystal cold field emission electron source operated at 5 kV. Images were collected using a mixed detector mode with upper and lower secondary electron detectors. HR-TEM images were taken using a FEI Tecnai F30 with Gatan multiscan charge coupled device (CCD) camera (MSC) for digital imaging with live Fourier transforms. The instrument operated at 300 kV using a cold field emission electron source. Also HR-TEM observations in the cross-sectional direction for the unaffected integrity of Pd deposited on the TiO₂ film were required for the better understanding of the crystallinity of the Pd. Thus, the conventional cross-sectional TEM specimens were prepared. The two specimens were bonded face-to-face with the epoxy. The epoxy used was M610 bond. The preparation steps of mechanical grinding, dimpling, and ion milling followed after this. As shown in Fig. 3a, the major requirement of selectivity of the deposition step is fulfilled; the Pd seeds are confined to the orthogonal lines and completely absent from the interline areas. The cross-sectional magnified image of the Pd pattern in Fig. 3b shows that Pd nanoparticles were uniformly deposited in the pattern. The particle diameter of the Pd nanoparticles was estimated to be about 5 nm, and the lattice spacings of 3.8902 Å were observed, which
agreed with those from JCPDS data. (Fig. 3c) Also, from the selected area diffraction pattern of the particles, the crystal structure of the Pd nanoparticle showed single-crystalline fcc structure and no other phase was found (Fig. 3d). The activity of the TiO\(_2\) photocatalyst will be lost during the process of Pd deposition. The reason for this is that, once Pd is deposited on the TiO\(_2\) top layer, a photocatalytic reaction will no longer occur, regardless of whether the irradiation is continued or not. Therefore, it is understood that an ultrathin Pd metallic layer may be formed on the surface of the TiO\(_2\). It was confirmed from inductively coupled plasma (ICP) atomic emission spectroscopic measurements that ca. 1.5 \(\times 10^{-7}\) g/cm\(^2\) Pd was adsorbed onto the TiO\(_2\) thin film in this process. This amount was sufficient to initiate the ELD.

For the ELD of ZnO, the Pd-patterned substrate was soaked in an aqueous solution of Zn(NO\(_3\))\(_2\) (0.05 M) and DMAB (0.01 M) at 55°C for 30 min. The solution of zinc nitrate and DMAB was transparent during the reaction, and hence deposition occurred via heterogeneous nucleation on the Pd catalyst particles attached to the substrate. After the surfaces with the attached Pd catalyst were fully covered with ZnO, no more ZnO particles grew with further soaking, probably because ZnO cannot work as a self-catalyst as happens in the case of ELD of Cu.

Figure 4 shows SEM images for 20 \(\mu\)m wide microlines (Fig. 4a) and 20 \(\mu\)m diam microdot arrays (Fig. 4b) of ZnO obtained by selective ELD on the TiO\(_2\) substrate. The microlines and microdots were composed of ZnO particles of about 200 nm in diameter (Fig. 4c), which grew in a direction normal to the substrate surfaces displayed in Fig. 4d. The surface profilometry of the 20 \(\mu\)m wide ZnO lines (measured by Tencor P-10) is shown in Fig. 5. The thickness of the particulate film was measured to be about 0.1 \(\mu\)m. Atomic force microscopy measurements gave an estimated standard deviation of the surface roughness (rms) of about 30 nm (not shown). Furthermore, as shown in Fig. 6, the ZnO film indicated a randomly oriented polycrystalline structure. The diffraction peaks can be indexed to be a wurtzite structure of ZnO.

Figure 7 shows photoluminescence (PL) spectra excited from ZnO samples as-deposited and after heat-treatment in an ambient atmosphere at 150, 300, and 600°C for 2 h using an He-Cd laser (325 nm). For the as-deposited sample, broad visible-light luminescence (500-800 nm) centering at 520 nm (green color) was observed. In addition, for the sample annealed at 300°C, a strong emission at \(\sim 380\) nm was observed. Of the sample annealed at 600°C, the UV emission weakened to one-seventh that of the sample annealed at 300°C. While the UV emission corresponds to near-band emission due to the recombination of bound excitons, the green emission peak is commonly referred to as deep level emission due to
impurities and native defects such as interstitial zinc atoms in the ZnO crystal.\(^2\) The origin of the green emission is controversial and several mechanisms have been proposed.\(^2\)-\(^5\)

Significant UV luminescence was observed in the samples annealed above 150°C, and its intensity was found to vary with the annealing temperature. The top peak intensity of the UV luminescence is plotted as a function of the annealing temperature in the inset of Fig. 7. The intensity of the UV luminescence increased at 150-300°C, peaked at 300°C, and decreased at 300-600°C, with increasing annealing temperature.

Conclusions

In conclusion, we fabricated UV light-emitted ZnO micropatterns on a glass substrate at 55°C by combining the ELD and photocatalytically activated TiO\(_2\) surfaces. Although further refinement is needed, the results demonstrated here show that low-temperature ELD is a viable technique for manufacturing light-emitting devices for ZnO optoelectronic applications.

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References