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Surface discharge that induces non-equibrium 2-dimensional plasma was employed to deposit ZnO film on PET substrate. The discharge energy was easily tuned by controlling the grid pattern on the electrode as well as the input AC bias. After irradiating a plasma to the precursor pre-coated on a substrate for a few minutes, hexagonal ZnO single phase was obtained. The crystallization was restricted within the selective area adjacent to the plasma to leave a clear step after washing the substrate in water. The technique was further developed into a direct patterning in a film formation.

ZnO is a very attractive material for electrical and optical devices, such as LED, solar cell and so on. Recently, much attention has been paid to ZnO as one of the alternatives to ITO for a transparent conductive oxide film. Various techniques were investigated to deposit ZnO film, such as magnetron sputtering,[1-4] pulsed laser deposition,[5, 6] chemical vapor deposition,[7, 8] ion plating,[9, 10] sol-gel,[11] and spray pyrolysis deposition.[12] However, most of these techniques require a high temperature annealing process to obtain well crystallized ZnO films, which locks out cheap plastic substrates for their practical use.

We focused on surface discharge technique under ambient pressure to deposit oxide films. Since non-equibrium 2-dimensional plasma is induced in discharge within the grids on the electrode, a plasma irradiation can be done to the selective and preferred area on the surface of the substrate below 200 °C.[13-16] Therefore, this technique will be developed into a convenient tool for a direct patterning in a film formation. We have already reported SnO_2 film formation by this technique.[16] However, in the conventional electrode for discharge, AC bias was applied from the front to the back of an insulating plate to induce inhomogeneous filamentary plasma due to a blurred screen printed metal grid on the plate, remaining large amount of precursor and/or intermediate products within the film. We adopted a coplanar grid type electrode to solve these problems. Local sparks in discharge was suppressed with a clear in-plane grid pattern formed by photo resist on a commercial epoxy plate, and then a homogeneous planar plasma was induced on the insulating plate attached on the grids.

In this paper, we fabricated a coplanar grid type electrode, and the discharge energy was optimized by tuning the grid pattern as well as the input AC bias to the electrode. We applied this technique to deposit ZnO films in air or in O_2 gas flowing. The technique was further developed into a direct patterning tool in a film formation.

The pectinate metal grid pattern as shown in Fig. 1 (a) was printed on a commercial epoxy photo resist substrate by exposing an ultraviolet light on it. Fig. 1 (b) shows a schematic representation of the cross section of the electrode for discharge. A cover glass or a zirconia

insulating plate (18 mm × 18 mm × 0.15 mm in size) was attached to the grid on the epoxy plate with a silicone adhesive sealant (TSE3941, MOMENTIVE) to fabricate the electrode. Fig. 2 shows the electric circuit to measure the discharge energy generated on the electrode. A sinusoidal wave from a function generator (WF1965, NF Co.) was applied to the electrode through a high-voltage power amplifier (Model 20/20C, Trek Inc.) up to 15 kV and 20 kHz. When AC bias exceeded the threshold level, a discharge was observed on the electrode, and a typical rhombic Lissajou figure was displayed on the monitor of a digital oscilloscope (TDS2024B, Tektronix Inc.).[17] The discharge energy is almost comparable to that stored in the capacitor, and then calculated from the area of Q-V diagram in the figure.

ZnO film was synthesized by surface discharge technique. 0.15 M of zinc nitrate hexahydrate (99 % purity, Wako Pure Chemical Industries, Ltd.) ethanol solution with some amount of additional 28 % aqueous ammonia (Wako Pure Chemical Industries, Ltd.) was prepared for a precursor solution. After forming an uniform liquid membrane of the precursor solution on PET substrate (25 mm × 25 mm × 1 mm in size) by a spin coating method at 2000 rpm, the substrate was dried in air and set on the holder to face with the electrode for discharge with the gap of 0.1 mm between them as shown in Fig. 3. 2-dimensional plasma was induced in discharge on the electrode, and then the plasma irradiation was done to the precursor pre-coated on the substrate for 3 minutes. The electrode temperature was kept below 80 °C by a cooling water unit on the back to prevent an overheating in discharge.

The characterization of the film was carried out by X-ray diffraction using CuKα radiation (RINT Ultima III, Rigaku Co.). The surface morphology was observed by an atomic force microscope (VN-8010N, Keyence Co.). The optical and electrical property was measured by a spectrophotometer (V-570, JASCO Co.) in the visible region, and Hall System (HMS-3000, ECOPiA Co.) using van der Pauw method, respectively.

High discharge energy is supposed to induce an active plasma in an atmosphere. In order to increase the discharge energy, the optimum metal grid pattern on the electrode was

designed.[16, 18, 19] Fig. 1 (a) shows a schematic representation of the grid pattern on the epoxy plate, where "W" and "L" is the width along the metal grid line and the distance between grids, respectively. The discharge energy was measured with varying both W and L at the constant AC bias of 11 kV and 5 kHz. Fig. 4 shows the discharge energy as a function of the metal grid pattern on the electrode. We employed a commercial cover glass for an insulating plate in this study. The energy was increased with W, the width along the grid line, and reached the maximum value at W=1.5 mm, attributing to the enhancement of the electron density on the electrode in discharge. However, the energy was decreased with wider W above W=1.5 mm due to the restriction in the electrode size. On the other hand, the energy was increased with decreasing L, the gap between grids. The minimum gap between grids was not less than 0.5 mm due to the resolution of the commercial photo resist in this study. By optimizing the grid pattern, the maximum energy of 1.3 J/s was generated at W=1.5 mm and L=0.5 mm. Fig. 5 shows the photograph of the electrode in discharge in air at AC bias of 11 kV and 5 kHz. Since O_2 gas plasma was almost clear, homogeneous blue plasma originated from N_2 gas in air was observed in the whole area between the pectinate metal grids.[20]

The energy was further increased by replacing an insulating plate to that with higher relative dielectric constant. As a consequence of the increase in the relative dielectric constant, approximately from 7 to 30 at 1 MHz for a cover glass and a zirconia plate, respectively, the discharge energy was enhanced and reached the maximum value of about 2.5 J/s, which is almost twice as that from the conventional cover glass. The energy is much higher than that of zinc nitride hexahydrate precursor to be decomposed completely within a few seconds. The discharge energy also depends on AC bias applied to the electrode. Fig. 6 shows the discharge energy as a function of AC voltage and frequency applied to the electrode covered with a zirconia insulating plate and the grid size of W=1.5 mm and L=0.5 mm. A dielectric breakdown was detected at the input AC voltage of 11 kV, and the abrupt increase of the energy was measured with voltage. The energy was also enhanced with frequency, and then reached

the maximum value of 4.7 J/s at 13 kV and 8 kHz. Due to a lower durability of the electrode, further input power gave damage to metal grids and brought an unstable discharge, declining the energy.

ZnO films were synthesized by irradiating the highest energy plasma to the precursor at AC bias of 13 kV and 8 kHz. Fig. 7 shows XRD pattern of films deposited in air with the electrode with (a) a cover glass and (b) a zirconia plate. After the plasma irradiation, a trace of the hexagonal ZnO (002) peak was detected with a large amount of intermediate products for the film deposited with the electrode (a), indicating that very little plasma in air reached the precursor, which was not enough to decompose the precursor completely. On the other hand, the intermediate products disappeared and hexagonal ZnO single phase was obtained for the film deposited with the electrode (b) with higher discharge energy. Since the surface temperature of the electrode in discharge was kept below 80 °C with a cooling water, a simple thermal reaction seems not to be the main process in the decomposition of the precursor. The crystallinity of ZnO phase was further improved for the film deposited in O_2 gas flowing at 10 L/min. As the intermediate products in the film deposited with the electrode (a) has a hydroxyl group as one of the ligands, the decomposition, or the oxidation of the precursor contains a hydrolysis process under the plasma irradiation.[12, 21] An oxygen plasma, or an active ozone generated in the film formation in O_2 gas flowing is supposed to enhance the hydrolysis process to promote the oxidation of the precursor.[16, 22, 23] The lattice constants of the film deposited here were calculated to a=3.25±0.004 Å and c=5.19±0.010 Å, which is almost comparable to those of JSPDS (36-1451). Although the film was opaque with lower transmittance of 63 %, the electrical resistivity was reduced to 4.1×10^{-3} Ω·cm without any dopant. Further optimization is required for the film to be a transparent conductive film.

Fig. 8 shows AFM image of the film deposited in O_2 gas flowing with the electrode covered with a zirconia plate. By washing the film with water after the plasma irradiation, a typical step with the difference in level of approximately 300 nm was observed, although the

step was distorted due to the lower resolution along the grid on the electrode. The step was produced along the edge of the grid line on the electrode, where the plasma decayed rapidly at a short distance to keep the precursor still on the substrate. The residual precursor was easily removed by washing the substrate with water, and then the crystallized step was left on the substrate. The technique was further developed into a direct pattering tool in a film formation. Fig. 9 (a) and (b) shows the photograph of the electrode in discharge with a grid pattern displaying the symbol of Shizuoka University, and the film deposited with the electrode (a) in O_2 gas flowing, followed by washing the substrate with water, respectively. An image of Mt. Fuji and Suruga bay consisted of ZnO film was imprinted on PET substrate like a seal mark. At this moment, the image is not so clear due to a microscopically inhomogeneous plasma, attributing to a low resolution of the handmade grid pattern on the commercial photo resist epoxy electrode. However, since the grid is easily designed to any configurations to induce plasma within the selective area and shape, the process will be developed to be a convenient tool for a direct pattering in a film formation.

In summary, surface discharge technique was developed to deposit ZnO film on PET substrate. The discharge energy reached the maximum value of 4.7 J/s at AC bias of 13 kV and 8.0 kHz. The energy corresponds to that to decompose the precursor completely in a few seconds. An active plasma induced on the electrode promoted the crystallization of hexagonal ZnO, and left a step on the glass substrate after removing a residual precursor by washing with water. Since the substrate temperature is kept below 80 °C in the film formation, the low melting materials are acceptable in this system. Additionally, the technique has many common features with a plasma display panel, therefore, surface discharge technique will be further developed to a novel tool for a film formation.

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Fig. 1

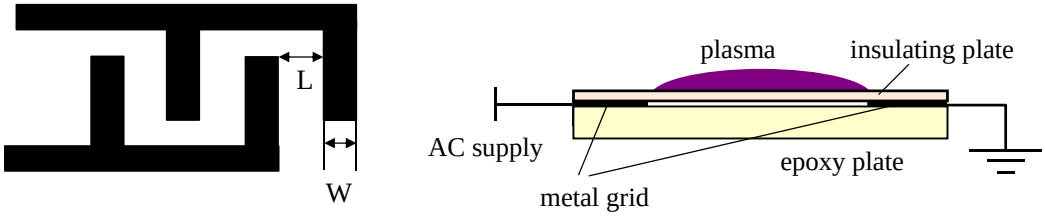

Fig. 1 Schematic representation of the electrode for discharge; (a) the metal grid pattern on the epoxy plate for a coplanar type, where "W" and "L" is the width of the metal grid and the distance between grids, respectively, and (b) the cross section of the electrode.

Fig. 2

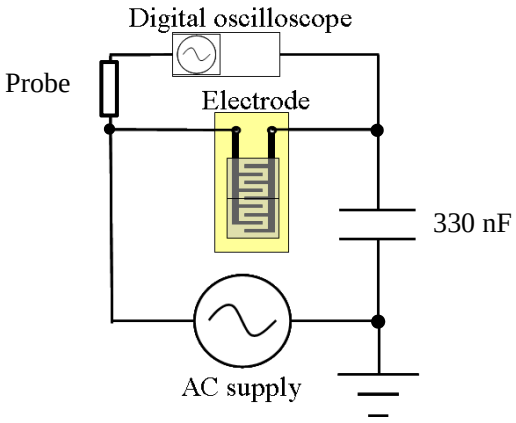

Fig. 2　Electric circuit to measure the discharge energy generated on the surface of the coplanar grid type electrode.

Fig. 3

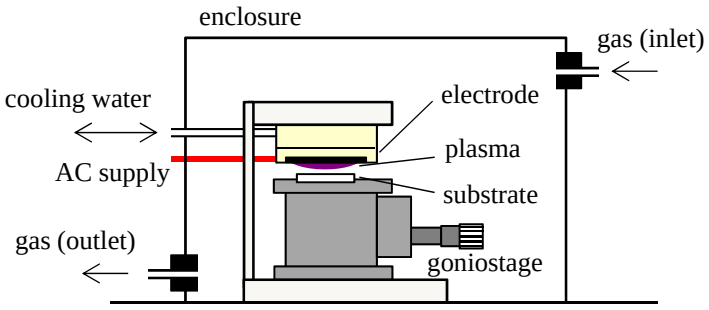

Fig. 3 Schematic representation of the film formation system by surface discharge technique.

Fig. 4

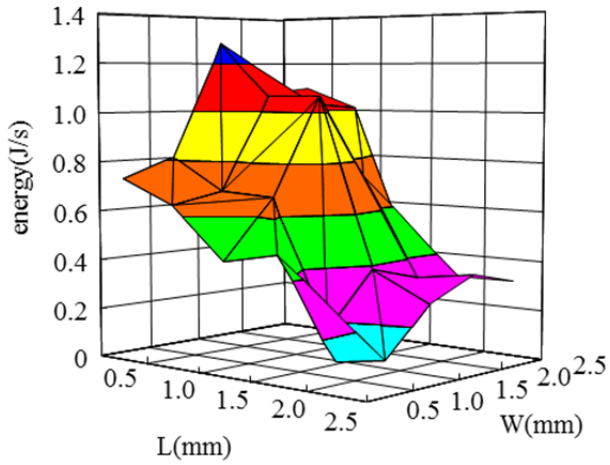

Fig. 4 Discharge energy as a function of the width of the metal grid, “W”, and the distance between grids, “L” at AC bias of 11 kV and 5 kHz. A cover glass is attached to the metal grid on the epoxy plate for the electrode.

Fig. 5

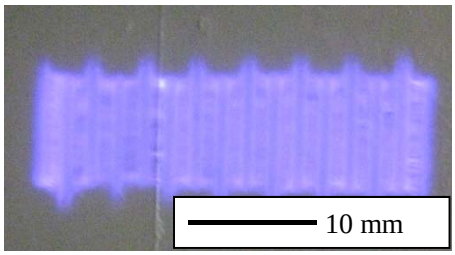

Fig. 5 Photograph of the electrode in discharge in air at AC bias of 11 kV and 5 kHz.

Fig. 6

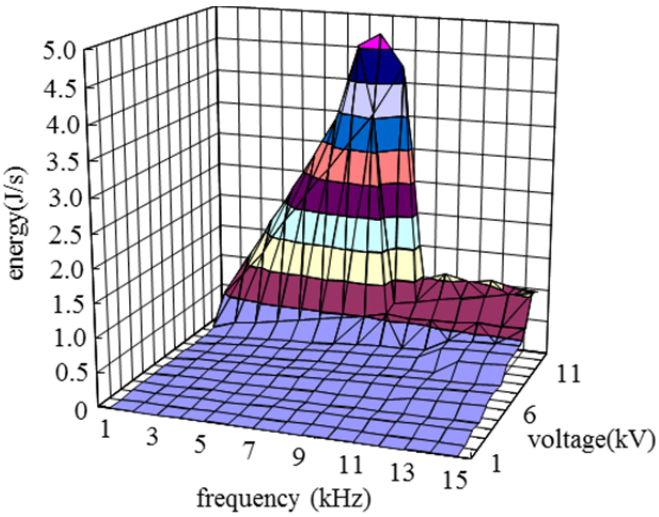

Fig. 6 Discharge energy as a function of voltage and frequency applied to the electrode covered with a zirconia plate on the grid pattern of W=1.5 mm and L=0.5 mm.

Fig. 7

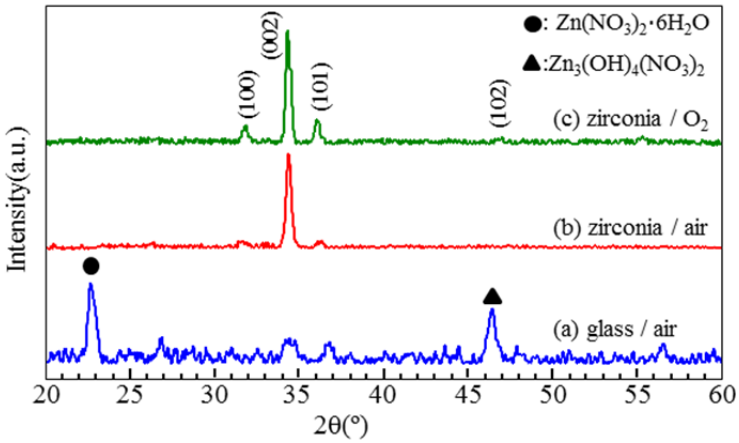

Fig. 7 XRD pattern of the film prepared in air with the electrode covered with (a) a cover glass, and (b) a zirconia plate. The pattern of the film prepared in O_2 gas flowing with the electrode covered with (c) a zirconia is also shown here.

Fig. 8

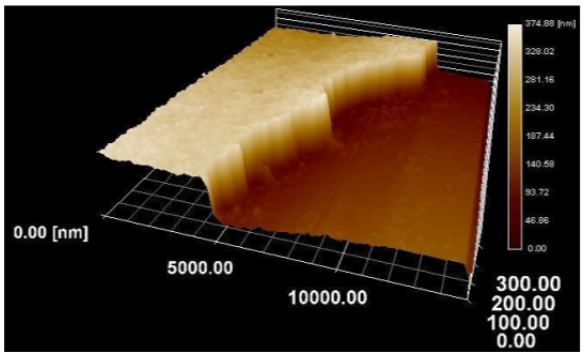

Fig. 8 AFM image of the film deposited on PET substrate in O_2 gas flowing with the electrode covered with a zirconia plate. The substrate was washed with water after the plasma irradiation.

Fig. 9

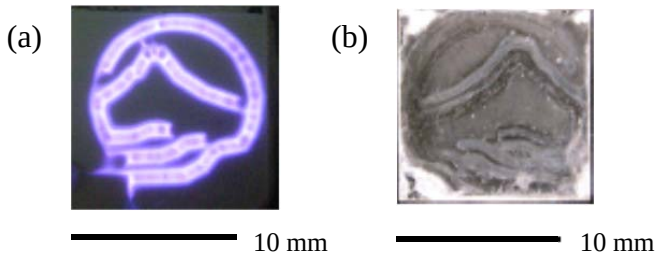

Fig. 9 Photograph of (a) the electrode in discharge with a grid pattern displaying the symbol of Shizuoka University, Mt. Fuji and Suruga bay, at AC bias of 11 kV and 5 kHz, and (b) the film deposited with the electrode (a) in O_2 gas flowing, followed by washing the substrate with water.