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# Enhancement of Ga-doped zinc oxide film properties and deposition rate by multiple deposition using atmosphere pressure plasma jet

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ABSTRACT

Multilayer film with an interfacial buffer layer made of different material has been show to improve the film properties. However, it is not well understood if similar benefits may be achieved by multiple deposition of GZO without the addition of new interfacial materials. Here we prepared single-, double-, and triple-deposited GZO films on glass substrate (preheated to 180 °C) by atmosphere pressure plasma jet (APPJ). We found that the triple-deposited film exhibits overall enhancement over the single-deposited film in deposition rate (110 nm/min) and the key properties, such as resistivity ($9.4 \times 10^{-4}$ Ω cm), crystallite size (16 nm), carrier concentration, mobility, and band gap. In particular, the resistivity and deposition rate are significantly improved by 33% and 35%, respectively. The results are attributed to the mitigation of lattice-mismatch between the film and the glass substrate by the bottom thin GZO film. The findings may also be applied to other deposition methods with moving nozzle or moving stage such as spray pyrolysis.



## 1. Introduction

Zinc oxide is a transparent and wide bandgap semiconductor [1–3] that has received widespread attention over the past decades in fields of optoelectronic devices such as liquid crystal devices, solar cells [4], light-emitting devices [5] and flat panel display [6] due to its lower cost and its relative richness in the crust of earth [7], compared to indium tin oxide (ITO), another widely used opto-electronic material. The gallium-doped zinc oxide (GZO) thin film has become one of the popular transparent conductive oxide materials, owing to its excellent optoelectronic characteristics, and gallium is an effective n-type dopant in ZnO because the covalent bond length of Ga–O (1.92 Å) is almost equal to that of Zn–O (1.97 Å). Hence, there is smaller lattice deformation in gallium doped zinc oxide, and the crystallinity is better than other dopant elements.

Zinc oxide thin films have been prepared in several methods such as magnetron sputtering [8], pulse laser deposition [9], metal–organic chemical vapor deposition [10], and spray pyrolysis [11]. Among those, sputtering is the most common technique and produces high quality films. However, since it is operated in vacuum, its cost is relatively higher than those without vacuum, and the size of its samples is limited by the vacuum chamber. Atmosphere pressure plasma jet, by contrast, is a non-vacuum and effective chemical vapor deposition technique, and provides a low temperature process with the help of plasma to initiate the chemical reaction. In APPJ methods, the area of substrate is much larger than the range a single jet can cover. Therefore, the nozzle must scan through the entire substrate to complete one pass of deposition, and the trajectory and number of passes significantly affect the film properties.

Multilayer deposition is one of the methods to improve both optical and electrical properties due to the high conductivity and high transparency that are provided by each layer [12,13]. Besides, some studies discovered that the down-layer or interfacial buffer layer thin films can provide better growth conditions such as lower lattice-mismatch, lower thermal expansion and the lowest surface energy for up-layer thin films and improve the overall crystallinity [14–17]. However, the multilayer deposition often requires using different material as the buffer layer, which may increase the process time, tool complexity and materials cost. The feasibility of enhancement of film properties and deposition rate by simple multiple deposition without buffer layer is still not well explored. In this paper, we compared the properties between single-, double-, and triple-deposited GZO thin films. We adjust the scanning speed and number of passes to achieve the multi-deposited process, and the deposition time is the same for all cases.

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## 2. Experimental details

### 2.1. Film deposition

GZO thin films were deposited under ambient atmosphere on glass substrates (Asahi Glass Co. Ltd, RLO-0.5, soda-lime alkali glass, 50 mm × 50 mm × 1 mm in dimensions) by APPJ. The schematic of APPJ, developed by Industrial Technology Research Institute (ITRI), is shown in Fig. 1. The details of the apparatus have been described in our previous papers [18,19]. The system consists of a plasma jet, a direct current (DC) pulsed power source, an ultrasonic generator, a hot plate and computer-controlled *x-y-z* stage. The DC pulsed power source generates the plasma with $N_2$ main gas at 250 V, a repetitive frequency at 26.3 kHz, and a 26.7% duty cycle (the on/off duration time of the power is 8/30 μs), followed by a transformer with a ratio of 1:60 that amplifies the voltage to 15 kV. Zinc nitrate [$Zn(NO_3)_2$, J.T. Baker, 99.6% purity] and gallium nitrate [$Ga(NO_3)_3$, Alfa Aesar, 99.9% purity] were used as the precursor without further purification. The atomic percentage, Ga/(Ga + Zn), was set at 8%. Pure deionized water is used as solvent and the concentration of the solution is kept at 0.7 M. The ultrasonic generator atomized the precursor at 2.45 MHz into mist, which was then injected to plasma region by carrier gas and experienced a chemical reaction. Nitrogen with a flow rate of 30 slm, is used as the main gas and the carrier gas is blended with 135 sccm $N_2$ and 45 sccm forming gas (93% Ar + 7% $H_2$). The distance between the nozzle and substrate is 2 mm and the pitch in the *y* axis is 2 mm. The power is set at 850 W and the substrate temperature is 180 °C. A single-deposited film is formed when the nozzle scans through the entire substrate once (one pass); a double-deposited film is formed when the nozzle scans through the entire substrate twice (two passes), and so forth. Accordingly the number of deposition is equal to the number of passes. To achieve higher deposition rate and better film properties, we study on the multi-deposited effect by adjusting scanning speed and number of passes. It is known that the deposition time = (C/scanning speed) × number of passes, where C is a geometrical factor of glass substrates size. Therefore, the deposition time remains consistent in this study. The conditions of deposition are summarized in Table 1.

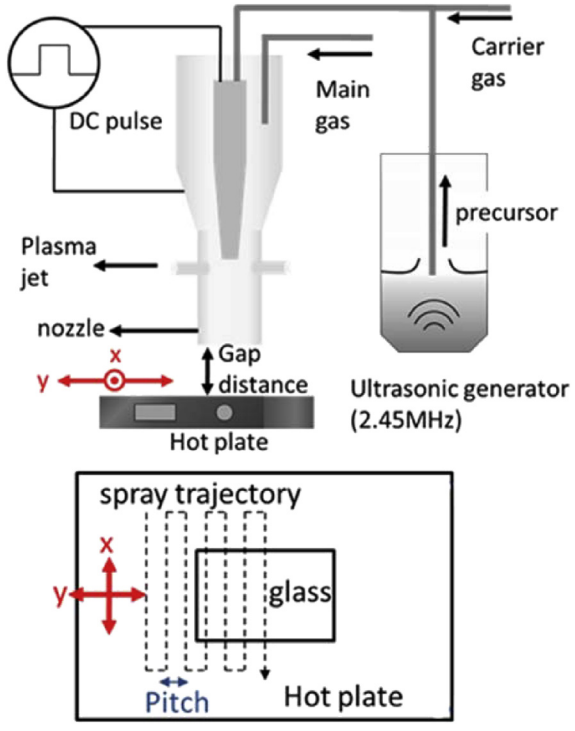


**Fig. 1.** Schematic of APPJ apparatus.

### 2.2. Film characterization

To characterize the crystallinity of thin films the grazing incidence X-ray diffraction (GIXRD, Rigaku TTRAX III) method with Cu Kα radiation (λ = 1.540598 Å) is used, with a grazing incidence of 0.5°, and a scanning range (2θ) of 25°–70°. The sheet resistance, Rs, of the films was measured by four-point probe method. The thickness of the films was measured by KLA-Tencor Alpha-step 500 surface profiler. The electrical properties were measured by Hall Effect (Ecopia HMS-3000) in the van der Pauw configuration at room temperature. The optical transmittances were measured by a UV–Vis spectrometer (Jasco V-670). Optical emission spectrum (OES, Horiba, Triax 320) was performed to investigate the species and chemical reaction in plasma in the wavelength from 200 nm to 1000 nm in order to better understand in the plasma reactivity. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Theta Probe) was used to analyze the chemical composition, in particular the changes of Zn binding energy. The films were etched ~80 nm by Ar ion beam sputtering for 150 s at 3 keV (beam current density: 1 μA/mm$^2$) before the measurement so that the interior of the films was measured. Secondary Ion Mass Spectrometer (SIMS, IONTOF, TOF-SIMS IV) was used to analyze the depth profile of GZO thin films, which provides detailed element distribution, in particular Ga content, across film thickness. During the data collection, the operating conditions were as follows: Analysis in $Bi^+$ gun with energy 25 keV and 1 pA, analysis area 100 × 100 μm$^2$, and the polarity was positive. The film was sputtered by $O_2^+$ gun ~6 nm a step with energy 1 keV and area 250 × 250 μm$^2$.

## 3. Results and discussion

OES measurement has been performed at approximately 2 cm downstream of the plasma jet exit to investigate the interaction between $N_2$ plasma and precursor. The emission spectrum from 200 nm to 1000 nm is shown in Fig. 2. The atomic gallium transition is observed at 403 nm, 416.5 nm, and the atomic zinc transition is observed at 471.5 nm, 480.5 nm, respectively [20]. These imply that the zinc and gallium-salt solution precursor are well-transformed. The presence of the excited nitrogen species, widely seen in nitrogen plasma [21–23], can be observed in the range of 300–390 nm (2nd positive system) [22]. We also observe the presence of $OH^-$ emission at 306–310 nm. In previous research, it is reported that $OH^-$ plays an important role in the conversion of Zn-salt solution to ZnO [24–26]. It is most likely that the reactive species in plasma, such as excited state $N_2$ and $N_2$ radicals, are involved in the conversion process.

**Table 1**
The conditions of deposition.

| Parameters | Unit | Conditions |
|---|---|---|
| Main gas (Plasma gas) | | Nitrogen |
| Carrier gas | | Nitrogen + (93% Ar + 7% $H_2$) |
| Main gas flow | L/min | 30 |
| Carrier gas flow | sccm | 135 ($N_2$), 45 (93% Ar + 7% $H_2$) |
| Scanning speed & number of passes | (mm/s) | (10,1), (20,2), (30,3) |
| Deposition power rate | W | 850 |
| Voltage | V | 250 |
| Duty cycle | μs | 8 on:30 off |
| Deposition time | s | 125 |