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Enhancement of ZnO nucleation in ZnO epitaxy by atomic layer epitaxy

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Abstract

Dry cleaning techniques employing argon, oxygen and hydrogen ECR plasma were used, respectively, to remove organic contaminants and native oxides on sapphire and silicon (Si) substrates prior to the growth of the ZnO film by atomic layer epitaxy. The cleaning efficiency was assessed by investigating the nucleation density and the incubation period for ZnO nucleation using scanning electron micrography (SEM) and Auger electron emission spectroscopic analysis (AES). ECR plasma pretreatment increased the ZnO nucleation density and reduced the incubation period for ZnO nucleation. Oxygen ECR plasma pretreatment was found to be more effective in enhancing ZnO nucleation than any other plasma pretreatment, and the effects are more prominent on the sapphire substrate than the silicon substrate. ZnO nucleation on the sapphire substrate is substantially enhanced by treating the substrate surface with oxygen ECR plasma prior to ZnO atomic layer epitaxy (ALE) because the hydroxyl packing density at the substrate surface is increased by oxygen plasma.

Keywords: ZnO; ECR plasma treatment; ALE; Epitaxy

1. Introduction

Zinc oxide films have long been investigated owing to their extensive and superior properties for practical uses. Recently, there is a considerable interest in growing high-quality epitaxial ZnO films on a practical substrate such as sapphire for short-wavelength optical devices including light-emitting diodes (LEDs) or laser diodes (LDs).

In the preparation of epitaxial ZnO films with high crystallinity, sapphire substrates of the *a*-, *c*- and *r*-axes have been widely employed due to its stability at growth temperatures. However, the sapphire substrates are unsatisfactory to be used as electrodes because of its high resistivity and are also expensive. In this point of view, silicon (Si) wafers are interesting for the substrates on which optical devices are fabricated. The Si wafer is an especially suitable substrate for ZnO growth because the thermal expansion coefficient of Si (3.57×10^{-6}/°C) is nearly equal to that of ZnO (4×10^{-6}/°C).

Atomic layer epitaxy (ALE) is a thin film growth technique allowing atomic-scale thickness control and usually occurs at a lower temperature than chemical vapor deposition (CVD). Typically ALE films are extremely smooth and conformal to underlying substrate surface. The ALE techniques produce ZnO films at relatively low temperature [1–4]. In ALE process, surface migration of precursors can be influenced by the process parameters such as diethyzinc (DEZn) and H_2O concentrations and substrate temperature. Moreover, impurities on substrates and reactivity of surfaces are factors that limit the surface diffusion of the precursors.

If native oxides and contaminants such as particles, organics and metallic impurities on the substrate surface are not removed completely prior to the epitaxial growth of a compound semiconductor such as ZnO, a film with a low quality will be obtained. In other words, a film with many defects such as a high density of dislocations, islands, pits and steps or a polycrystalline film will be obtained. Also, a lower nucleation density and thereby a lower film growth rate would be obtained without appropriate pretreatment of the substrate surface. Therefore, cleaning of the substrate surface prior to ZnO epitaxy

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is very important to grow a ZnO film with a good crystal quality and to enhance ZnO nucleation. In this study, we report the effect of the ECR plasma pretreatment on the initial growth of ZnO on sapphire (0001) and p-type Si (100) substrates by ALE.

2. Experimental

In this experiment, two kinds of substrates were prepared, one is a p-type Si (100) surface and the other is a sapphire (0001) surface. For the clean surface, the Si wafers were dipped in a 5% dilute HF acid solution and then rinsed in deionized water and sapphire wafers were chemically treated in a hot $3H_2SO_4$+H_3PO_4 solution and rinsed in deionized water. Then the substrate was dried by pure N_2 gas and loaded into the ECR plasma chamber. The Si and sapphire substrates were cleaned by treating with hydrogen, oxygen or argon ECR plasma. The process conditions for the plasma cleaning were as follows. Microwave power was 300 W at 2.45 GHz and the stainless steel cylindrical plasma chamber had a diameter of 160 mm and a height of approximately 150 mm. The gas flow rate was about 15 sccm and the substrate temperature was 298 K. The exposure time was 10 min. In the ECR chamber, the samples were positioned 20 cm below the center of the electromagnet. The base pressure of the ECR plasma chamber was 5×10^{-6} Torr, while the process pressure was approximately 5×10^{-3} Torr.

After the plasma treatment, ZnO films were deposited on Si and sapphire substrates using the ALE technique. Diethylzinc (DEZn) and H_2O were used as precursors for zinc and oxygen, respectively. The precursor reservoirs were at 5 °C. These source gases were alternately fed into the chamber through separate inlet lines and nozzles. The pulsing sequences of the pneumatic valves were controlled by a computer. The typical pulse lengths were 0.2 s for feeding DEZn, 2 s for feeding H_2O and 5 s for purging the reactants. Purge gas was nitrogen of high purity. The substrate temperature was 170 °C. The pressure in the chamber during the deposition was varied between 0.1 and 0.3 Torr. The deposition cycle number was varied in the range of 20–70. The schematics of the ALE system is shown in Fig. 1.

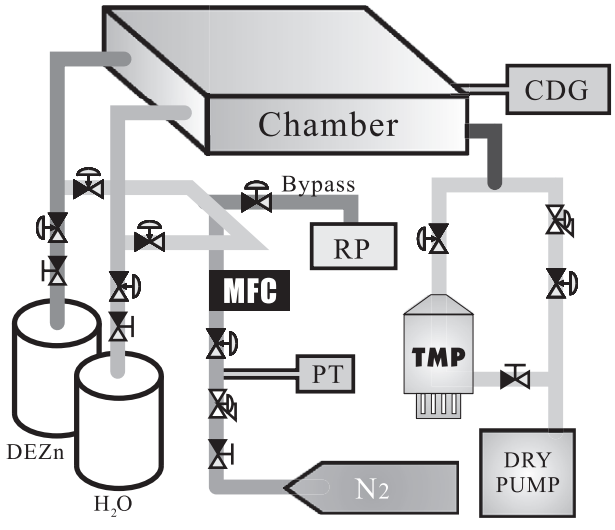

Fig. 1. A schematic of the ZnO ALE system.

The cleaning efficiency was assessed by investigating the incubation period for ZnO nucleation. The film growth has been measured by plan-view scanning electron microscopy (SEM). Also Auger electron emission spectrometry (AES) analysis was performed to compare the thicknesses and atomic concentrations of ZnO thin films.

3. Results and discussion

In ZnO ALE growth, the growth does not start immediately but there is an apparent incubation period for about 30–40 cycles [5]. We investigated the nucleation of ZnO on the substrates by comparing the incubation period for ZnO nucleation in the samples by scanning electron microscopy (SEM), even though the exact nucleation origin could not be investigated because of the limited resolution of SEM. Fig. 2a and b shows ZnO nucleation on the sapphire substrate by ALE with and without O_2 plasma pretreatment, respectively. Difference in ZnO nucleation density is not clearly seen after 40 ALE cycles between with and without O_2 plasma pretreatment, but a salient difference is noticed after 30 ALE cycles between the two.

We can see a lot of ZnO nuclei on the sapphire substrate treated with O_2 ECR plasma, while we can see nearly no nuclei on the one without ECR plasma treatment. By comparing these SEM analysis results we may say that the incubation period of ZnO nucleation on the sapphire substrate pretreated with O_2 ECR plasma is less than 30 cycles, while the one without ECR plasma pretreatment is in between 30 and 40 cycles. Also it may be said that ZnO nucleation is enhanced by O_2 ECR plasma pretreatment.

Detailed experimental data for ZnO nucleation on sapphire and silicon substrates are shown in Fig. 3a and b. The nucleation density values have been obtained by counting the number of nuclei in a fixed size of area in SEM images as described above. The overall data show a tendency that the ZnO nucleation density increases linearly as the ALE cycle number increases on both substrates for pretreatments of various kinds of plasmas although the data points somewhat deviate from linear distribution.

In the case of ZnO ALE on the sapphire substrate, nucleation-enhancing effects of four different ECR plasma pretreatments seem to be as follows: O_2 plasma>Ar plasma $\approx$ H_2 plasma $\gg$ no plasma. The incubation period is defined as the time required for nucleation to be initiated. Therefore, we can get the nucleation period of ZnO nucleation by extrapolating each data line down to zero nucleation density and reading the ALE cycle number at the zero nucleation density. The relative incubation periods of

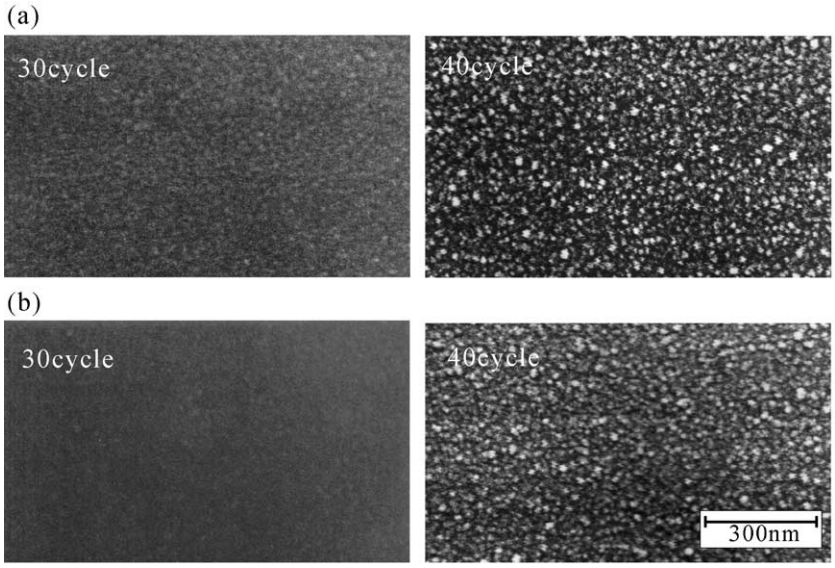

Fig. 2. Scanning electron micrographs of the ZnO thin films deposited on the sapphire substrate by ALE (a) with and (b) without O_2 plasma pretreatment for 30 and 40 cycles.

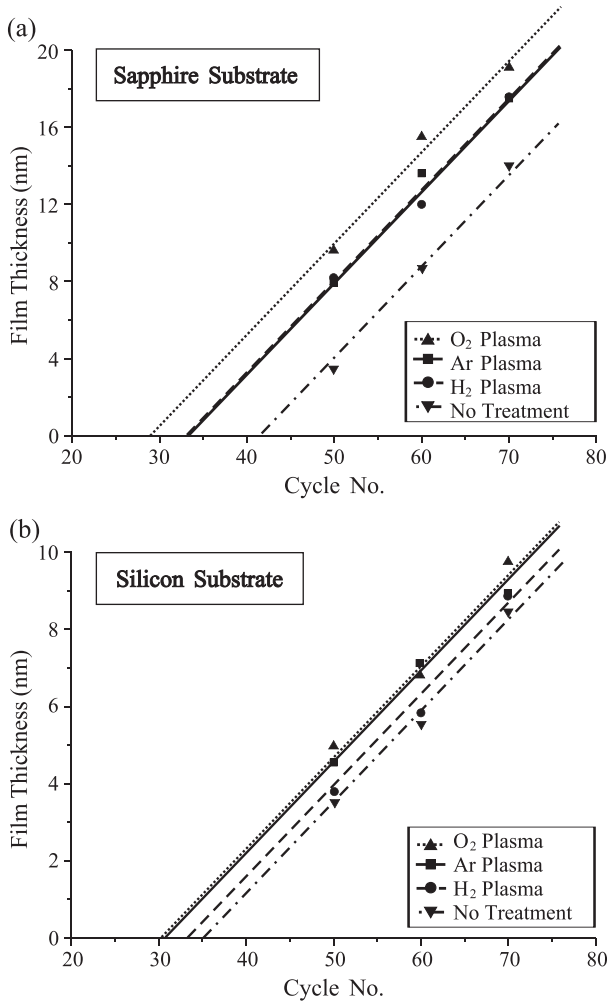

Fig. 3. Change of the thickness of the ZnO thin film deposited on (a) sapphire and (b) silicon substrates pretreated with different plasmas with ALE cycle number.

the ZnO nucleation for the four different ECR plasma pretreatments show the same trend as the relative nucleation densities since the slopes of all the data lines are the same. In other words the relative incubation periods are O_2 plasma<Ar plasma$\approx$$H_2$ plasma$\ll$no plasma.

ZnO ALE on the silicon substrate shows basically the same trend as that on the sapphire substrate in the order of different plasma treatments from the aspect of the nucleation-enhancing effect, but there is some difference. In the case of ZnO ALE on the silicon substrate, the ZnO nucleation-enhancing efficiency of the Ar ECR plasma pretreatment is almost the same as that of the O_2 ECR plasma pretreatment, while in the case of ZnO ALE on the sapphire substrate the ZnO nucleation-enhancing effects of the Ar ECR plasma pretreatment is almost the same as that of the H_2 ECR plasma pretreatment. The experimental results for ZnO nucleation on the silicon substrate are summarized as follows:

(the nucleation density)
O_2 plasma$\approx$Ar plasma>H_2 plasma$\gg$no plasma
(the incubation period for nucleation)
O_2 plasma $\approx$ Ar plasma>H_2 plasma$\ll$no plasma.

The ZnO nucleation-enhancing effects of the plasma pretreatment can be confirmed by AES analysis results. Figs. 4a–d are AES depth profiles of the ZnO thin films grown by ALE for 50 cycles on the sapphire (Al_2O_3) substrate, the surface of which were treated with (a) O_2 plasma, (b) H_2 plasma, (c) Ar plasma, and (d) without plasma. If we define the position at which the Zn and the Al curves intersect each other as the interface between the sapphire (Al_2O_3) substrate and the ZnO films, The ZnO film grown on the sapphire substrate treated with O_2 plasma (Fig. 4a) is the thickest. Next, the ZnO film grown on the

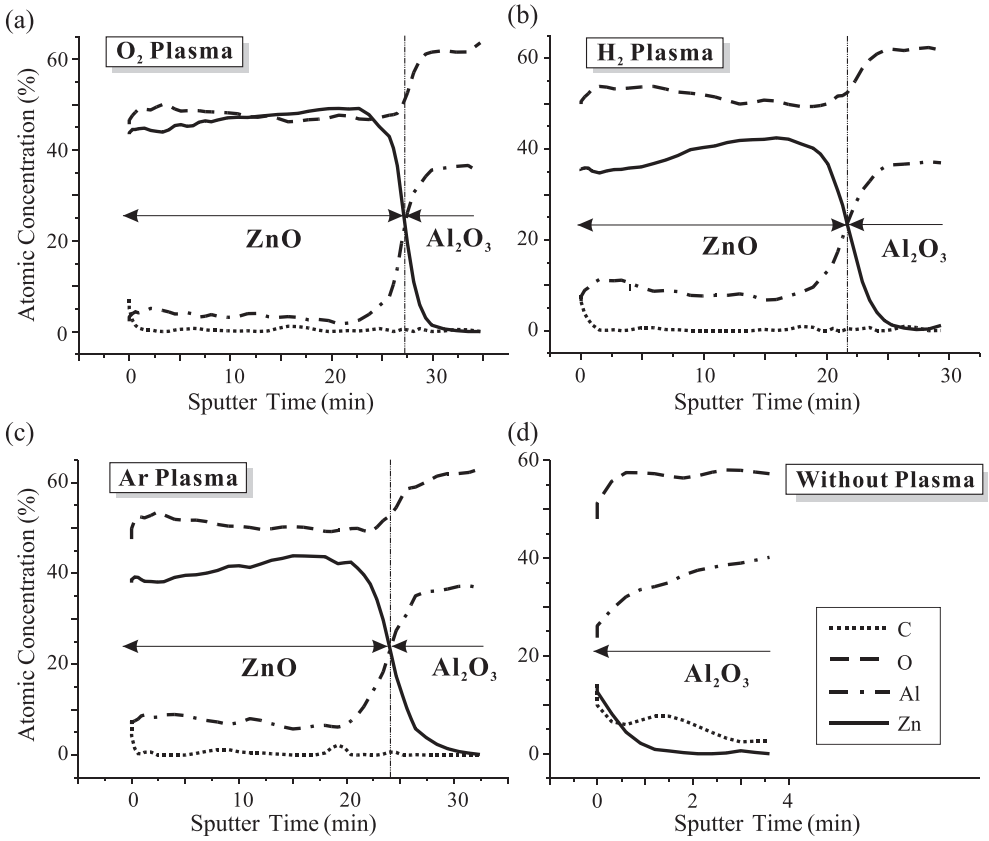

Fig. 4. AES depth profiles of ZnO thin films on the sapphire substrate pretreated with (a) O_2 plasma, (b) H_2 plasma, (c) Ar plasma and (d) without plasma (cycle no. 50).

substrate treated with Ar plasma (Fig. 4c) is slightly thicker than that that grown in the substrate treated with H_2 plasma (Fig. 4b). No ZnO film has been grown on the substrate not treated with plasma (Fig. 4d). Another thing to be noted is the concentration of aluminum in the ZnO film. If the ZnO film had been grown very ideally by ALE on the sapphire substrate, no aluminum would be detected in the ZnO film because a ZnO film grows in a layer-by-layer mode in ideal ALE. However, in our case the ALE process does not seem to have been ideal unfortunately. Actually, the ZnO films seem to have grown in a mode closer to a cluster mode. Therefore, the existence of aluminum in the ZnO film in the AES depth profiles indicates that the sapphire substrate is not completely covered with the ZnO film. In fact, 50 cycles may not be long enough for the ZnO film to cover the substrate surface completely. The coverage of the sapphire substrate surface by the ZnO film is highest in the case of O_2 plasma pretreatment. The coverage of the substrate treated with Ar plasma seems to be slightly higher than that of the substrate treated with H_2 plasma. An interesting thing is that the coverage of the substrate surface is consistent with the thickness of the ZnO film. We may conclude that O_2 plasma is the most effective in enhancing ZnO nucleation on the sapphire substrate because it offers the thickest ZnO film and the highest coverage of the substrate surface with the ZnO film for the same number of ALE cycles.

The AES depth profiles of the ZnO films grown by 50 cycles of the ALE process on the silicon substrate treated with different plasmas are shown in Fig. 5. Some distinct differences are found between Figs. 4 and 5. Firstly, the ZnO films grown on silicon are much thinner than those grown on sapphire (compare the sputter time indicating the film thickness). Secondly, the coverage of the silicon substrate surface by ZnO is much higher than that of the sapphire substrate surface by ZnO since no aluminum is detected in the ZnO films of the AES depth profiles. Thirdly, the ZnO film has grown on the silicon substrate not treated with plasma at all, whereas the ZnO film has not grown at all on the sapphire substrate not treated with plasma. In short, the ZnO nucleation-enhancing effect of the plasma pretreatment is not so strong on the silicon substrate. Also there is little difference in the ZnO nucleation enhancement among the three different plasma pretreatments, although the ZnO film grown on the silicon substrate surface treated with O_2 or Ar plasma is slightly thicker than that grown on the silicon substrate surface treated with H_2 plasma. All the AES analysis results discussed above agree well with the experimental results in Fig. 3a and b obtained by SEM images.

The mechanism that the plasma pretreatment enhances ZnO nucleation is not clear. Plasma surface treatment is generally known as a powerful process used to modify

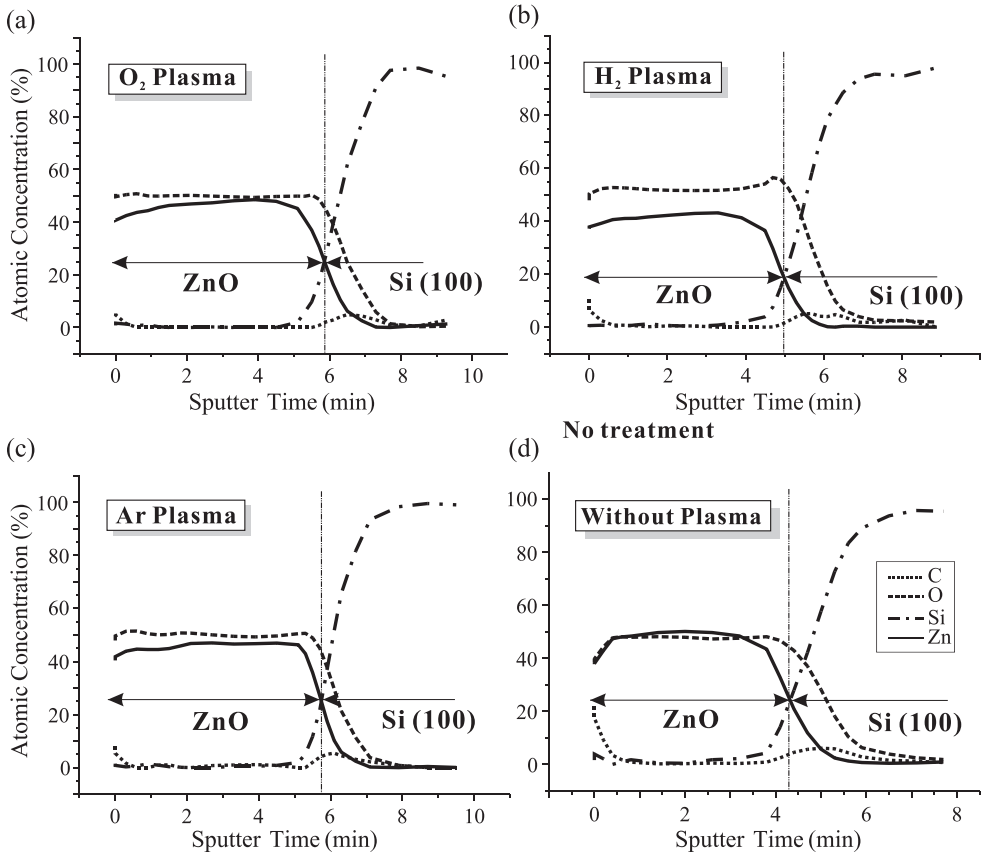

Fig. 5. AES depth profiles of ZnO thin films on the silicon substrate pretreated with (a) O_2 plasma, (b) H_2 plasma, (c) Ar plasma and (d) without plasma (cycle no. 50).

surface characteristics. Plasma pretreatments with different kinds of plasmas have been employed for sapphire substrate cleaning prior to ZnO deposition. Oxygen plasma pretreatment of Si and sapphire substrates using O_2 ion bombardment was attempted for ZnO growth on sapphire in this work. It is concluded that the surface pretreatment of sapphire substrates using O_2 plasma was crucial for growth of good-quality ZnO [6]. It was reported that O_2 plasma treatment resulted in clean surface suitable for ZnO epitaxial growth in the plasma-enhanced molecular beam epitaxy (PEMBE) of ZnO thin films on *c*-plane (0001) sapphire [7].

In this study, one possible explanation for the effect of O_2 plasma treatment in our ALE work and the reported PEMBE work is the increase of the hydroxyl group density on O_2 plasma-treated surfaces. A different density of hydroxyl groups would produce a different concentration of reactive surface sites. ZnO films were deposited by ALE using alternating exposures of the substrates to DEZn and H_2O [1–3]. The chemistry for the ALE growth of ZnO using these precursors has been known as [8]:

DeZn pulse:

$$\mathbf{S-OH} + \mathbf{Zn(CH_2CH_3)_2} \rightarrow \mathbf{S-O-Zn(CH_2CH_3)} + C_2H_6$$

Water pulse:

$$\mathbf{S-O-Zn(CH_2CH_3)} + \mathbf{H_2O} \rightarrow \mathbf{S-O-Zn-OH} + C_2H_6$$

where S denotes a surface site and species in bold letters are surfaces. The growth of ZnO based on these reactions is known to be surface reaction limited. In the case of the sapphire substrate, the substrate material on the surface of which initial ZnO growth occurs is sapphire. Therefore, we have many reasons to believe that the growth of ZnO on sapphire depends mainly on the atomic packing at the surface, especially the initial packing condition of hydroxyl on the sapphire substrate. According to the literature [9], water adsorption by sapphire surface includes both dissociative adsorption and molecular adsorption. At room temperature and normal pressure, the saturated hydroxyl coverage on the (0001) sapphire surface is only about $5\times10^{18}/m^2$ on average. This value is much smaller than that of Si surface. Therefore, we may conclude that oxygen ECR plasma treatment increases the hydroxyl packing density at the substrate surface.

4. Conclusion

In ZnO growth using ALE, epitaxial growth of ZnO (hexagonal symmetry) on the silicon or sapphire substrate depends mainly on the atomic packing at the surface, especially the initial packing condition of hydroxyl on the substrate. Different local packing densities result in different incubation periods for ZnO nucleation.

ECR plasma pretreatment reduces the incubation period for ZnO nucleation. Oxygen ECR plasma pretreatment is more effective in reducing the incubation period for ZnO nucleation by increasing the ZnO nucleation density than any other plasma pretreatment. Because the saturated hydroxyl coverage on sapphire surface is much smaller than that on silicon surface, ECR plasma pretreatment effects are more prominent on the sapphire substrate than on the silicon substrate.

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