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Enhancement of field emission of the ZnO film by the reduced work function and the increased conductivity via hydrogen plasma treatment

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The ZnO films deposited by magnetron sputtering were treated by H/O plasma. It is found that the field emission (FE) characteristics of the ZnO film are considerably improved after H-plasma treatment and slightly deteriorated after O-plasma treatment. The improvement of FE characteristics is attributed to the reduced work function and the increased conductivity of the ZnO:H films. Conductive atomic force microscopy was employed to investigate the effect of the plasma treatment on the nanoscale conductivity of ZnO, these findings correlate well with the FE data and facilitate a clearer description of electron emission from the ZnO:H films. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3167301]

ZnO is a promising candidate for applications in field emission (FE) displays because of its fascinating physical and chemical properties.[1,2] In previous reports, good FE characteristics of ZnO were usually attained in ZnO nanostructures by large geometric field enhancement due to their high aspect ratios.[2–5] An alternative method for improving FE characteristics is lowering work function by various surface-treatment processes, since electron emission is critically dependent on the nature of chemical species terminating the surface.[6] Furthermore, a heavy *n*-type doping can also enhance FE by lifting the Fermi level and lowering the work function.[7,8] Recently, it was reported that hydrogen doping significantly increased the free electron concentration and the conductivity of ZnO.[9–11] On the other hand, negative electron affinity (NEA) was often observed at the surface of various wide band-gap semiconductors (e.g., diamond, boron nitride) terminated with hydrogen atoms,[12–14] which allows easily for electron emission. Therefore, the introduction of hydrogen into ZnO may be one of the most potential methods for improving its FE. However, the FE characteristics of ZnO:H films was scarcely studied,[15,16] and the mechanism has not yet been clearly illustrated. In this study, we report that the FE of ZnO films is enhanced by H-plasma treatment due to the reduced work function and the increased conductivity of the ZnO:film.

The ZnO films were deposited on n^+-Si (001) substrates by a conventional radio frequency (rf) magnetron sputtering. To introduce hydrogen or oxygen intentionally, the ZnO films were directly immersed in a H/O plasma in a capacitively coupled rf plasma reactor. The details of growth and treatment conditions can be found elsewhere.[17]

The morphologies of ZnO films were characterized by Conductive atomic force microscopy (CAFM) with a NT-MDT Solver P47 using a Pt-coated Si cantilever. The current distribution image was achieved simultaneously by using the contact mode with a fixed force on the cantilever and recording the current for a fixed applied bias voltage of 8.0 V. The single point *I-V* curve was obtained by maintaining a constant tip/sample force and then varying the tip/sample bias voltage ranging from −10 to 10 V while measuring the cathodic current. The FE experiments were performed in an ultrahigh vacuum chamber with a base pressure better than 3×10^{-7} Pa at room temperature.

Secondary ion mass spectroscopy (SIMS) was used to investigate the distribution of hydrogen in the ZnO:H film. The depth profiles of the main elements in the ZnO:H film and Si substrate are shown in Fig. 1. It is evident that hydrogen exists in the ZnO film and diffuses into the entire film after H-plasma treatment. It has been reported that hydrogen can diffuse into ZnO films with a depth of more than several micrometers by H-plasma exposure.[18] In the present study, the thicknesses of the ZnO films are about 1 μm, hence hydrogen can diffuse into the entire film.

As demonstrated in our previous report,[17] the electrical properties of ZnO films were improved by H-plasma treatment. Hall measurement results show that the carrier concentration increases sharply from 10^{17} to $3\times10^{19}/\mathrm{cm}^3$, and the electron mobility increases from 15 to 35 $\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$ after H-plasma treatment. As a result, the conductivity of the ZnO:H film is more than three orders of magnitude larger than that of the as-grown ZnO film. On the contrary, the carrier concentration and mobility of ZnO are both reduced slightly after O-plasma treatment.

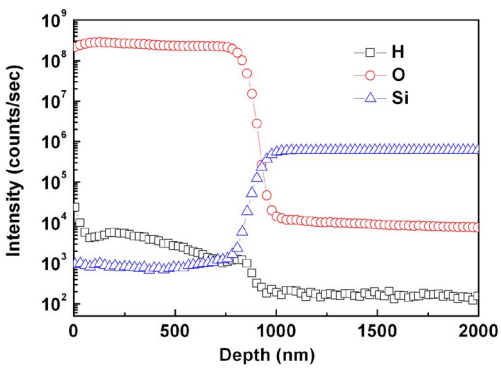

FIG. 1. (Color online) SIMS depth profiles of the H-plasma treated ZnO film on Si substrate.

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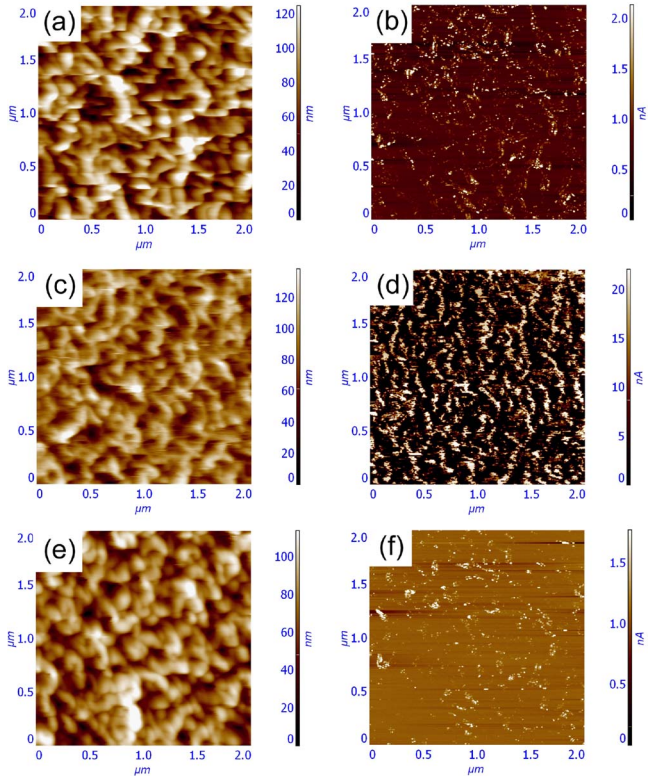

FIG. 2. (Color online) Topography (a, c, and e) and current images (b, d, and f) from a scan size of 2×2 μm^2 of the as-grown (a and b), the H-(c and d), and O-plasma (e and f) treated ZnO films, respectively.

To demonstrate the effect of the plasma treatment on the nanoscale conductivity of ZnO, CAFM measurements were carried out for the as-grown and H/O plasma treated ZnO films, and the corresponding topography [(a), (c), and (e)] and current distribution images [(b), (d), and (f)] are shown in Fig. 2, respectively. The as-grown ZnO film shows a small and sparse current distribution, and the current intensity and density increase significantly after H-plasma treatment, whereas both of them decrease slightly after O-plasma treatment. Assuming a threshold current of 1 nA, the percentages of conductive area α_C are calculated to be 2%, 17%, and 1.8%, corresponding to the as-grown, the H- and O-plasma treated ZnO films, respectively. Obviously, the enhanced conductivity by H-plasma treatment leads to more channels of electron transport, thus, the increased conductive area.

The typical local current-voltage (*I-V*) curves of these films were also measured and the results are presented in Fig. 3. As seen, the point contacts on the as-grown and O plasma-

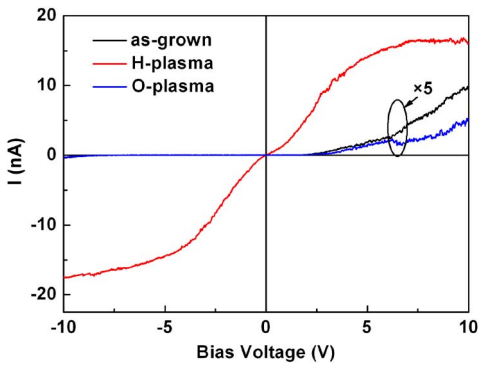

FIG. 3. (Color online) Typical local *I-V* curves of the ZnO films measured by CAFM before and after plasma treatment.

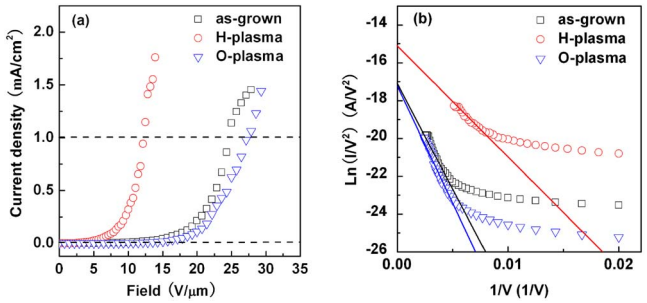

FIG. 4. (Color online) Electron FE characteristics of the ZnO films before and after plasma treatment: (a) The $J-E$ characteristics and (b) the corresponding FN plots $\ln(I/V^2)\sim 1/V$.

treated ZnO films result in nonlinear and rectifying *I-V* curves. This behavior is probably attributed to the Schottky contact created between the Pt-coated tip and the ZnO surface, since Pt has a high work function of 5.64 eV.[19] However, the H plasma-treated ZnO film exhibits a linear *I-V* behavior, except for a saturated characteristic at the higher voltages that is due to the limited saturation current (~20 nA) of the instrument. The electron concentration of the ZnO film is high enough after H-plasma treatment, electron tunneling is a dominant transport mechanism of current flow between the ZnO film and the Pt-coated tip even though the existence of barrier between of them.[20] As a result, the Schottky contact between the Pt-coated tip and ZnO is changed into Ohmic contact after H-plasma treatment, and much higher current flow through the Pt-coated tip and the H-plasma treated ZnO under the same bias voltage.

The electron emission characteristics of the as-grown and H/O plasma-treated ZnO films are shown in Fig. 4, respectively. Where the *J-E* characteristics are shown in Fig. 4(a) and the corresponding Fowler–Nordheim (F-N) plots are given in Fig. 4(b). The turn-on field E_{on} and the threshold field E_{th} are defined at an emission current density of 10 $\mu A/cm^2$ and 1 mA/cm^2, respectively,[20] as indicated by two dashed horizontal lines in Fig. 4(a). The E_{on} and E_{th} are found to be 9.8 and 24.4 $V/\mu m$ for the as-grown ZnO film, respectively. While the H-plasma treated ZnO film has the best FE characteristics with the lowest E_{on} of 3.6 $V/\mu m$, and the lowest E_{th} of 12.2 $V/\mu m$. These values are comparable with and even lower than the results attained from various ZnO nanostructures.[21,22] Evidently, the FE characteristics of the ZnO film are considerably improved after H-plasma treatment, while they are slightly deteriorated after O-plasma treatment (E_{on}=13.6 $V/\mu m$, E_{th}=24.7 $V/\mu m$).

In Fig. 4(b), the FN plots show a rough linear relationship in the high-voltage range for all the samples, implying that a quantum tunneling mechanism is responsible for the emission. For the FN emission, the current density obeys the FN equation[23]

$$\ln\left(\frac{I}{V^2}\right) = -\frac{B\phi^{3/2}d}{\beta}\frac{1}{V} + \ln\left(\frac{\alpha A\beta^2}{\phi d^2}\right), \tag{1}$$

where A and B are constants, I and α are the emission current intensity, the effective emission area, respectively. ϕ, d, and V are the work function, the distance between the anode and the cathode, and the voltage applied to the samples, respectively. The β is the field enhancement factor related to the surface morphology, which reflects the ability of the emitters to enhance the local electric field. The AFM images of the

ZnO films, as shown in Figs. 2(a), 2(c), and 2(e), indicate that the surface roughness and morphologies of the ZnO films treated with H/O plasma are almost similar to those of the as-grown sample. Since the morphologies of the ZnO films are not changed very much after plasma treatment, we reasonably assume that the β values of the three samples are the same. Therefore, the variation in the slope $k=-B\phi^{3/2}d/\beta$ of FN plots reflects the change in the work function ϕ of ZnO films since d remains unchanged. According to the FN plots in Fig. 4(b), and taking the work function ϕ of the as-grown ZnO film as 5.3 eV,[21] the work function ϕ is estimated to be 3.75 and 5.50 eV for the H- and O-plasma treated samples, respectively. In comparison with the as-grown ZnO film, the work function of the H-plasma treated sample is reduced by as much as 1.55 eV.

As mentioned previously, H-plasma treatment significantly improves the conductivity of ZnO films with much higher carrier concentration. This heavy n-type doping can reduce the work function of the ZnO film by up-shifting their Fermi level. This shift is estimated to be about 0.4 eV according to the relationship of electron concentration and the Fermi level.[7] Obviously, the smaller shift of Fermi level cannot explain the observed reduction of the work function of 1.55 eV alone. On the other hand, a lower and even NEA was usually observed at the surface terminated with hydrogen atoms for various wide band-gap semiconductors, e.g., diamond[12] and boron nitride.[13,14] Therefore, we propose that the larger reduction of the ZnO work function mainly be attributed to the decrease of the electron affinity resulted from the H-terminated surface of ZnO.

As can be seen from Eq. (1), for a given β, ϕ, and d, the intercept $b=\ln(\alpha A\beta^2/\phi d^2)$ of FN plots reflects the variation of effective emission area α.[23] In this work, β and d remain unchanged and α is normalized to 1 for the as-grown ZnO film. By taking the β values determined from the slope above, α is calculated to be 5.8 and 0.9 from the intercept of the FN plots in Fig. 4(b) for the H- and O-plasma treated samples, respectively. The effective emission area is slightly decreased after O-plasma treatment, whereas it is significantly increased after H-plasma treatment, which may be understood according to the three-step FE model.[24] According to the model, the emitted electrons are assumed to subject a three-step process involving internal emission, electron transport, and vacuum emission.[24] At the first step (internal emission), electrons are injected into the conduction band of ZnO films from n^+-Si substrates. At the second step (electron transport), the injected electrons transport across the ZnO films, which is directly limited by the conductivity of the films. Moreover, at the third step (vacuum emission), the electrons emit into vacuum at the surface of the ZnO films by tunneling through a surface barrier, which depends on the local field enhancement factor and the ZnO work function. The effective emission area is determined by the three steps connected in series. In the present work, because the Si substrates are heavily doped, electrons can be easily injected from substrate to ZnO by tunneling, the influence of the internal emission on FE can be neglected. At the second step, the CAFM results show that H-plasma treatment leads to the increased conductive area, thus the most injected electrons can transport through the ZnO films. At the last step, though the field enhancement factor remains unchanged, the work function of ZnO reduces significantly after H-plasma treatment, which makes the transported electrons emit easily. Consequently, the enhanced conductivity, together with the reduced work function of the ZnO:H films, leads to the increase of the effective emission area.

In conclusion, a significant enhancement of FE from the ZnO:H film has been observed, and the E_{on} is reduced from 9.8 to 3.6 V/μm after H-plasma treatment. The improvement of FE characteristics is attributed to the reduced work function and the increased effective emission area. The increased effective emission area is related to the reduced work function and the enhanced conductivity of the ZnO:H film, while the decrease of work function is due to the lifting of the Fermi level and the H-terminated ZnO surface. Additionally, the CAFM results show that the nanoscale conductivity of ZnO:H is obviously enhanced because of tunneling emission due to H-plasma treatment.

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