Fabrication and Performances of Different Nano-Electrode Materials on Diamond Thin Film

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Abstract. Diamond/Al doped ZnO (AZO) nanowire composite films and diamond/ indium tin oxide (ITO) nanowire composite films were separately grown on silicon substrates by using plasma chemical vapor deposition techniques and vacuum electron beam evaporation techniques. And the structures and morphologies of the as-deposited thin films were characterized by means of energy diffraction spectrum (EDS), X-ray diffraction spectrum (XRD), field emission scanning electron microscope (FE-SEM) and surface resistance tester. The experimental results indicate that AZO nanowires films and ITO nanowires films are made on the diamond substrates, respectively. The crystallinity of AZO films and ITO films is both fairly high, and the diameters of nanowires are both uniform. The average diameters of the nanowires is about 30nm of AZO and 50nm of ITO. And the corresponding film resistivity was 8.0×10⁻⁴Ω·cm and 2.0×10⁻⁴Ω·cm respectively. The feature of AZO nanowire and ITO nanowire grew on diamond films, which act as nano-electrodes, played an important role in further improving the surface resistance performances of diamond.

1. Introduction

In recent years, several types of nanostructures including nanowires, nanoparticles and nanotubes, have been developed rapidly by exploiting their unique optical, electrical, chemical, physical, mechanical, and piezo-electrical properties [1-4]. The field of nanowires is one of the high interest area for researchers and industry [5-7]. A nanowire is a nanostructure, which possesses a characteristic ‘acicular’ like structure in a few nanometers wide [8-10]. With the development of optical and electric devices, controllable nanowires are becoming increasingly important.

Transparent conducting films are now widely used in a variety of optoelectronic devices, such as touch panels, photovoltaics, transparent thin film transistors, light emitting diodes, solar cells and flexible displays [11-13]. Owing to its excellent optical-electrical properties, indium tin oxide (ITO) is the predominant transparent conductive oxide (TCO) used in various kinds of optoelectronic devices. However, there is a strong demand for cheap, and efficient alternatives [14]. Al doped ZnO (AZO) is such a promising TCO compound.

ZnO films are the most attractive functional transparent conducting materials, which have a small capacity, so they can function as electron conducting pathway and efficient mechanical support because of their high conductivity, chemical stability and mechanical flexibility [15-20]. People choose different materials (such as carbon cloth [11], glass [12], fluorne-doped tin oxide [17], sapphire [18], diamond films [19], Cu [20] etc.) as a substrate for the preparation of ZnO transparent conductive film. Owing to the diamond film has a series of excellent physical and chemical properties, in microelectronic, mechanical processing, optics and other fields have widely application prospect. In the device to join diamond film contributes to the improvement of the stability, the heat conduction
performance and the working life of the device. As far as we know, until now, although there are some reports about the growth of transparent conductive nanowire [21-23], but few comparative study on AZO nanowire and ITO nanowire transparent conductive films, which were deposited on the diamond substrate, growth behavior and photoelectric properties. How to hold the diamond thin film dielectric properties at the same time, and make its surface conductive even transparent conductive to the improvement on the performance of the photoelectric device has significant research value. Therefore, making a thorough comparative study on the structure of diamond/AZO nanowire composite films and diamond/ITO nanowire composite films are essential not only for explaining the growth mechanism but also to extend the potential applications of diamond based nano-electrode devices in optoelectronic fields.

In this paper, diamond/AZO nanowire composite films and diamond/ITO nanowire composite films are fabricated, respectively, where microwave plasma chemical vapor deposition (MPCVD) technique was combined with an electron beam evaporation deposition (EBED) technique. And the surface morphologies, microstructure and electrical performances of the as-deposited AZO and ITO nanowires films electrodes were characterized. The growth mechanism of AZO and ITO nanowires was discussed.

2. Experimental
The diamond film layer was grown on the silicon substrate by MPCVD system. In order to obtain more nucleation points, the silicon wafer was pretreated in suspending liquid of diamond powder with alcohol in an ultrasonic cleaning machine prior to the deposition of the diamond layer. Then the silicon substrate was put into a quartz chamber. The typical parameters used for the MPCVD process are given in table 1.

| MPCVD process parameters | Values  |
|--------------------------|---------|
| CH₄/H₂/sccm              | 1/100   |
| Substrate temperature/°C | 900     |
| Total gas pressure/kPa   | 7.1     |
| Microwave power/W        | 1500    |
| Plasma processing time/h | 12      |
| Thickness of film (μm)   | 5       |

Table 1. Process parameters are employed for the MPCVD process of diamond layers.

Table 2. Process parameters are employed for the EBED process of AZO and ITO thin films.

| EBED process parameters | Values  |
|-------------------------|---------|
| Target materials/ZnO:Al₂O₃ | 98:2    |
| Beam current (mA)       | 30      |
| Vacuum (Pa)             | 2×10⁻²  |
| Substrate temperature (°C) | 400   |
| Voltage (V)             | 6000    |
| Filament current (A)    | 0.7     |
| Oxygen gas flow(sccm)   | 4       |
| Thickness of film (nm)  | 600     |
| EBED process parameters     | Values     |
|----------------------------|------------|
| Target materials/In$_2$O$_3$:SnO$_2$ | 9:1        |
| Beam current (mA)          | 20         |
| Vacuum (Pa)                | 2.9×10$^{-2}$ |
| Substrate temperature (°C) | 365        |
| Voltage (V)                | 6000       |
| Filament current (A)       | 0.7        |
| Oxygen gas flow (sccm)     | 8          |
| Thickness of film (nm)     | 600        |

After that, electron beam vapor deposition (EBED) method was utilized for AZO film and ITO film electrode layer deposition on the diamond film, respectively. The thickness of the electrode layer is 600nm controlled by films thickness monitor. The typical parameters used for the EBED process are given in table 2, respectively. Need of special note is here, AZO films and ITO films both experimental process conditions were optimized. Specific optimization process is as follows: first, a series of AZO films and a series of ITO films were deposited on glass substrates by using EBED equipment, through the structure properties of the films, transmittance and resistivity characteristic testing and comprehensive comparison, to determine the optimum process conditions both of AZO film and ITO film. And the optimum process conditions are showed in table 2, respectively. Figure 1 shows the transmittance curves of an AZO film and an ITO film. Both of AZO film and ITO film were deposited on glass substrate under the optimum process conditions, respectively. And the corresponding film resistivity is 2.5×10$^{-4}$Ω·cm and 6.2×10$^{-5}$Ω·cm respectively.

![Figure 1](image_url)

**Figure 1.** Transmittance curves of the AZO thin film and ITO thin film (both the thickness of the films is 600nm)

The surface morphologies, microstructures and surface resistances of AZO and ITO thin films deposited on diamond layer was characterized by X-ray diffraction (XRD) spectrum, field emission scanning electron microscope (FE-SEM) and surface resistance tester.

3. Results and Discussions

Fig. 2 show the XRD spectrum of the diamond/AZO composite thin film samples. Although the intensity of the ZnO (112) peak is the strongest, the diamond peaks still appear with relatively low intensity. Peaks presented at 43.9° and 75.3° are assigned to the (111) and (220) diffraction peaks from the diamond substrate. Similarly, the energy diffraction spectrum (EDS) of AZO films shows that
appear C, O, Al and Zn characteristic peak. The XRD spectrum of the diamond/ITO composite thin film is shown in Fig.3. The strong In$_2$O$_3$(222) peak can be seen, the diamond peaks are similar to the above-mentioned case.

![XRD spectrum of the AZO thin film sample deposited on diamond layer](image1)

**Figure 2.** XRD spectrum of the AZO thin film sample deposited on diamond layer

![XRD spectrum of the ITO thin film sample deposited on diamond layer](image2)

**Figure 3.** XRD spectrum of the ITO thin film sample deposited on diamond layer

Fig.4 (a), (c), (e) and (b), (d), (f) show the SEM images of the AZO and ITO nanowires fabricated on the diamond substrates, respectively. The AZO and ITO nanowires are disordered and not parallel, but which have uniform diameters. The average diameters of the nanowires is about 30nm of AZO and 50nm of ITO.
Figure 4. FE-SEM images of the AZO and ITO films deposited on diamond layer, where panels (a), (c) and (e) are for AZO films deposited on diamond layer, and panels (b), (d), (f) are for ITO films deposited on diamond layer, respectively.

The growth mechanism gained an understanding of considering the periodic atomic arrangement of AZO and diamond (or ITO and diamond). We thought that AZO on diamond has a geometrically appropriate epitaxial relationship that reduces the stress energy of the AZO (or ITO) lattice. The growth both of the AZO and ITO nanowires are progressing through the tip, which is in agreement with the nanonail work by Michael M. Oye et al.[20] Although the lattice mismatch between the AZO and diamond, is a significantly larger, a possible epitaxy relationship would be proposed because the
two type structures can form an energetically favorable periodic coincidence lattice at the interface [19]. In such cases, the AZO nanowires may grow straight up. But in other regular conditions, such as without an energetically favorable periodic coincidence lattice at the interface, the nanowires could not be similar fashion to trees: straight up. This seems to be the reason why the nanowires grow disorderly.

The surface resistivities of the diamond/AZO and diamond/ITO composite films were measured by a surface resistance meter, which was $8.0\times10^{-4}\,\Omega\cdot\text{cm}$ and $2.0\times10^{-4}\,\Omega\cdot\text{cm}$ respectively. Obviously similar to ITO nanowire film, the conductivity of AZO nanowire film, act as nano-electrodes on a diamond substrate, is also very high.

4. Conclusions
In summary, diamond/AZO nanowire composite films and diamond/ITO nanowire composite films are made, respectively, by using the microwave plasma chemical vapor deposition technique and the electron beam vapor deposition technique. And the crystallinities of the AZO nanowires and ITO nanowires are both fairly high. In addition, the feature of the AZO and ITO grown on diamond films, which act as nano-electrodes, played a major role in further improving the surface resistance performances. So there are the application prospect of diamond/AZO and diamond /ITO composite devices is very broad in optoelectronic fields.

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