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Improved field emission properties from metal-coated diamond films ☆

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Abstract

Diamond films were prepared by microwave plasma chemical vapor deposition (MWPCVD). In order to obtain better field emission properties, the samples coated with different metals were prepared. The results showed that the field emission properties of diamond coated with metals could be greatly improved in comparison to pure diamond film and the different kinds of coated metals have different influences on the field emission properties. The possible reasons of effects on the field emission properties are discussed, which were probably due to the reduced effective surface work function by metal coatings, but the detail of the mechanism should be studied further. The surface morphology and microstructure of the sample were characterized by Atomic Force Microscope (AFM), X-ray photoelectron spectroscopy (XPS), X-ray Diffraction (XRD) and Raman spectrum tests.

Keywords: MWPCVD diamond films; Metal coatings; Field emission properties

1. Introduction

The electron field emission properties of carbon-based materials have been studied and used for cold cathodes of field emission displays (FEDs) [1]. Since the negative electron affinity (NEA) of the diamond was discovered by Himpsel [2], as well as superior properties such as chemical inertness, mechanical hardness and thermal stability, much attention has been paid to diamond films as one of the most promising materials for field emitters [3–5].

But due to the high resistivity of diamond, the replenishment and transport of electrons in bulk diamond are diminished and thus reduce electron emission of diamond. Compared to other carbon-based materials such as amorphous carbon and carbon nanotubes, directly deposited CVD diamond films generally require higher threshold fields and exhibit smaller emission currents for field emission [6–9]. Therefore, it is imperative to improve the emission properties of diamond films with respect to field emitters used for FEDs.

Metal–diamond interfaces could be used for solving the above problem, by means of metallic surface coatings which could result in a reduced positive electron affinity (PEA) or even induce a negative electron affinity (NEA). P.K. Baumann et al. studied the interface properties of metal (Cu, Co, Zr etc.)–diamond with respect to field emission characteristics [10,11]. By employing ultraviolet photoemission spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) measurements, possible mechanisms that these metals could induce an NEA surface on differently textured natural single crystal diamond films were presented. Only few reports on emission from metal–polycrystalline diamond interface have been presented. Joseph D. Shovlin et al. [12] studied electron emission from MWPCVD diamond films coated with gold layers. In this paper, field emission properties from different metal (Ti, Al, Mo, Ni) coatings on MWPCVD polycrystalline diamond films were systematically studied. The results indicate that field emission properties could be significantly improved by a metal coating compared to the as-deposited diamond film. Possible reasons are discussed, considering the characteristics of surface morphology and microstructure of the prepared samples.

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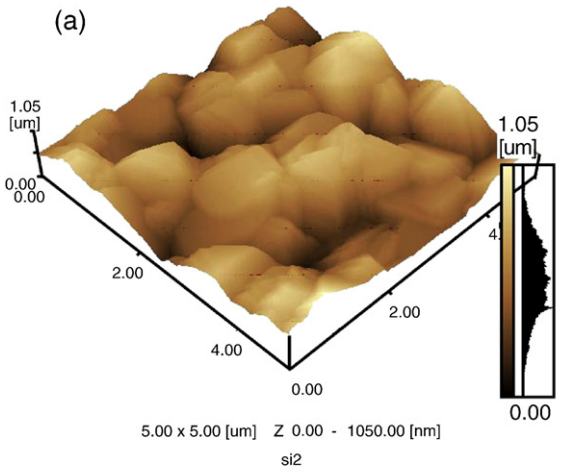
2. Experimental

The substrates were as-received polished n-Si (100) wafers, with resistivity of 0.008–0.02 Ω cm. Prior to deposition, the substrates were polished by WC powders for 30 min, in order to get a rough surface. Then they were ultrasonically scratched in a suspension of diamond abrasive grease dissolved in ethanol for 1 h to obtain the crystal seeds on the surface, which could contribute to the growth of diamond grains. In a final step, they were in turn ultrasonically cleaned in ethanol and DI water for 20 min and then dried with N_2. The diamond films were deposited on these pretreated substrates by means of microwave plasma chemical vapor deposition with base pressure of 3.0×10^{-3} Pa in the CVD reaction chamber. The source gas was a mixture of hydrogen and methane with flow rates of 100 sccm and 1 sccm, respectively. During the deposition time of 2 h, the total pressure of 5.5 kPa was maintained and the substrates temperature of 800 °C was kept at microwave power of 1500 W. Diamond film prepared under the above experimental conditions was p-type diamond which had been confirmed by using the thermal probe method. Magnetron sputtering was used for metal deposition on surface of diamond films which had been pretreated by hydrogen plasma, high purity (99.99%) metal as deposition target. During the sputtering process, the current and pressure were maintained at 1A and 1 Pa, and substrate temperature was kept at room temperature. The thickness of metal layer was controlled by sputtering time. Different metal coatings (Ti, Al, Mo, Ni) were deposited by means of magnetron sputtering with the same thickness of about 30 nm (the thickness of the metal layer was estimated by ex situ XPS). The surface morphology and microstructure of the diamond films were examined by AFM, XPS, XRD and Raman. The micromorphology of the films before and after metal deposition was examined and shown in Fig. 1. Electron field emission properties were measured using a parallel plate diode structure under the pressure of about 6×10^{-5} Pa. The deposited film and phosphor coated ITO film were used as cathode and anode respectively and the interelectrode spacer was an insulating layer with thickness of 100 μm.



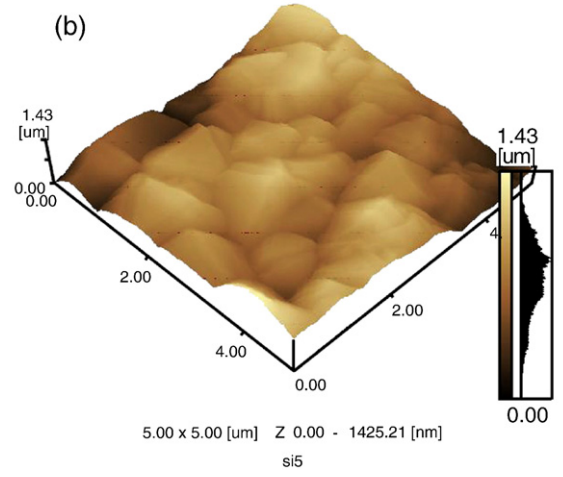


Fig. 1. AFM of the samples: (a) the as-deposited diamond and (b) diamond film with metal coating.

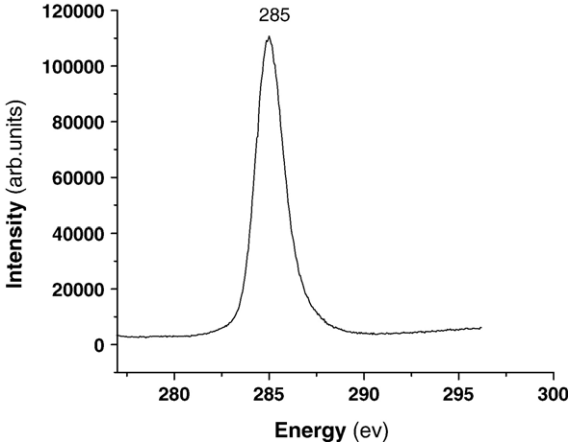


Fig. 2. XPS of the prepared diamond film.

3. Results and discussion

The average size of diamond grains and the thickness of film are evaluated according to AFM measurements of the samples

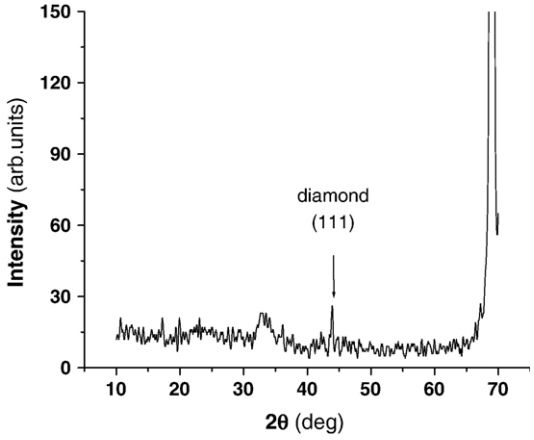


Fig. 3. X-ray diffraction spectrum of the prepared diamond film.