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Effect of metallic seed layers on the properties of nanocrystalline diamond films

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ABSTRACT

Three metallic films (Mo, Ti and W) were sputtered on Si substrates and ultrasonically seeded in diamond powder suspension. Nanocrystalline diamond (NCD) films were deposited using a dc arc plasma jet CVD system on the seeded metallic layers and, for comparison, a seeded Si without any metallic layer. The effect of metallic seed layers on the nucleation, microstructure, composition and mechanical properties of NCD films was investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy and nanoindentation. We found that the metallic seed layers were transformed into metallic carbide or/and metallic silicide during the deposition of NCD films at high temperature. Adding metallic seed layers had no obvious effect on the bonding structure of the NCD films but significantly improved their surface roughness and mechanical properties. The NCD film deposited on W seed layer displays the lowest root-mean-square roughness of 19 nm while that on Ti seed layer has the highest compactness, hardness and elastic modulus.

1. Introduction

Diamond is an interesting material in the fields of micro-electromechanics, tribology, electronics, biology and medicine because of its superior mechanical, optical, thermal and electrical properties [1]. Especially, possessing the highest acoustic velocity as well as the highest thermal conductivity, diamond is nearly an ideal substrate material for high frequency and high power surface acoustic wave (SAW) application [2–5]. High frequency SAW device cannot be fabricated directly using polycrystalline diamond (PCD) films which usually have the large grain size and high surface roughness, because the lithography technology in device fabrication process requires low surface roughness of substrate. The surface roughness of PCD film can be reduced by mechanical polishing. Unfortunately, polishing is a time consuming, complex and costly process. On the other hand, nanocrystalline diamond (NCD) and ultra-nanocrystalline diamond (UNCD) films represent good alternatives to PCD films for fabricating SAW devices without the necessity of post-polishing process because of their nano-scaled grains and remarkable surface smoothness [6]. Furthermore, the use of NCD and UNCD can eliminate large acoustic wave propagation loss and provide the elastic properties of NCD and UNCD that were not inferior to high-quality PCD or even single crystal diamond [7]. Large acoustic wave propagation loss is expected in PCD due to the acoustic scattering at large angle grain boundaries, especially if the lateral grain dimensions are close to acoustic wavelengths (about 1 μm) and SAW device apertures and transducer separations.

UNCD films suffer from a poor thermal conductivity and low elastic modulus because of a relatively high fraction of sp2-bonded carbon connecting the grains and a high renucleation rate during growth [8]. However, NCD films have thermal conductivity and elastic modulus as high as single crystal and microcrystalline bulk diamond. This is because they grow typically at initially high nucleation site densities and have significantly lower amounts of sp2-bonded carbon trapped at defects or grain boundaries [9]. Therefore, NCD films are more suitable for the high frequency and high power SAW devices as compared to UNCD films.

Minimizing the surface roughness of NCD films and optimizing their elastic properties are required in high frequency and high power SAW device application. Numerous substrate pretreatment techniques have been used to enhance the nucleation densities and reduce the surface roughness of NCD films, such as substrate mechanical abrasion, ultrasonic particle treatment and bias enhanced nucleation (BEN) [10]. Also, it has been shown that metallic nucleation layers can promote the nucleation of NCD due to an improved embedding of ultrasonically introduced nanosized diamond seeds on the nanometer rough metallic surfaces and a rapid carburization of the metallic surfaces during the early stages of diamond film formation [8,11]. However, few works reported on the effect of metallic nucleation layers on the properties of NCD. Recently, the effect of Cr underlayer on the structure, microstructure, composition,

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and elastic properties of NCD films was reported [12], but no similar study has been done on other metallic seed layers such as Mo, Ti and W.

In this study, NCD films were deposited on bare Si and three metallic (Mo, Ti, W) seed layers over Si using a dc arc plasma jet CVD system. The prepared NCD films were characterized to ascertain the effect of the metallic seed layers on the nucleation, topography, composition, microstructure and mechanical properties.

2. Experiments

In order to enhance the nucleation and improve the properties of the NCD films such as the adhesion to the substrate, the surface roughness and the grain size, molybdenum (Mo), titanium (Ti) and tungsten (W) layers of about 200 nm thickness were deposited onto mirror-polished silicon (Si) wafers by radio frequency magnetron sputtering metallic targets (diameter: 60 mm, purity: 99.99%) in high-purity (99.99%) argon (Ar) gas. The Ar flows metered using appropriate mass flow controllers are 20 sccm. The Si wafers have been ultrasonically cleaned in deionized water, acetone, alcohol, and deionized water in sequence, and finally dried with nitrogen (N_2) flow. The sputtering process lasted for 10 min with the power of 100 W, the pressure of 2 Pa and the target-substrate distance of 50 mm.

As a seeding treatment for nucleation enhancement prior to NCD deposition, the prepared metallic layers over Si and a bare Si wafer were ultrasonically treated for 2 h in NCD powder suspension mixed with acetone and dimethylsulfoxide, followed by an ultrasonically rinsing in deionized water. The NCD powders are commercial ultrafine diamond prepared using detonation method and their particle size, confirmed by a transmission electron microscope (TEM, JEOL JEM-2100), is about 5 nm.

Following this, NCD was deposited on the seeded samples by dc arc plasma jet CVD using a gas mixture of methane (CH_4), Ar and hydrogen (H_2). Gas flows are 0.2 slpm for CH_4, 1.5 slpm for Ar and 1.5 slpm for H_2, respectively. The substrate temperature was monitored by an infrared pyrometer and was kept at about 900 °C. The chamber pressure was maintained at 4.0 kPa and the arc power was 8 kW. The deposition time of the NCD films was 2 min for nucleation research and 60 min for growth study.

The surface topography and morphology of the metallic seed layers and NCD film growth were characterized using atomic force microscopy (AFM, Agilent 5500 from Agilent) operated in tapping mode with Si cantilevers and scanning electron microscopy (SEM, JEOL JSM-6700F). The crystalline phases were identified by X-ray diffraction (XRD, Rigaku D/MAX III-C) using a diffractometer with CuKα radiation (40 kV, 40 mA, $\lambda = 0.15406$ nm). The pole figures were measured to confirm the possible fiber texture of NCD by XRD (Rigaku SmartLab). Microstructural analyses of the diamond deposits were performed by micro-Raman spectroscopy using a diode-pump solid state (OPSS) laser ($\lambda = 532$ nm) (Thermo DXR Raman Microscope). The mechanical properties of NCD films were tested by nanoindentation technique (MTS nano indenter XP system), and the hardness and Young's Modulus of the NCD films were determined using the continuous stiffness measurements (CSM) method.

3. Results and discussion

The AFM topographical images of the three sputtered metallic layers and bare Si are shown in Fig. 1. Round shaped and uniform grains were observed on all the three metallic films. Among these metallic films, W film shows the lowest surface root mean square (RMS) roughness of 1.5 nm (Fig. 1a), followed by Mo film (about 1.7 nm) (Fig. 1c), and the Ti film possesses a little rougher surface of 3.2 nm (Fig. 1b). The bare Si without any metallic layers is extremely smooth with RMS roughness of 0.8 nm (Fig. 1d) smaller than that of metallic layers.

Fig. 2 is the AFM images of the metallic layers and bare Si ultrasonically seeded in NCD powder suspension. Single NCD particles and agglomerates are observed embedded in the surfaces of metallic films (Fig. 2a–c). Note that the seeds are mostly embedded as single NCD particle in the metallic film surfaces, especially in W film surface (Fig. 2c). Larger NCD agglomerates are formed on the surface of bare Si, and the

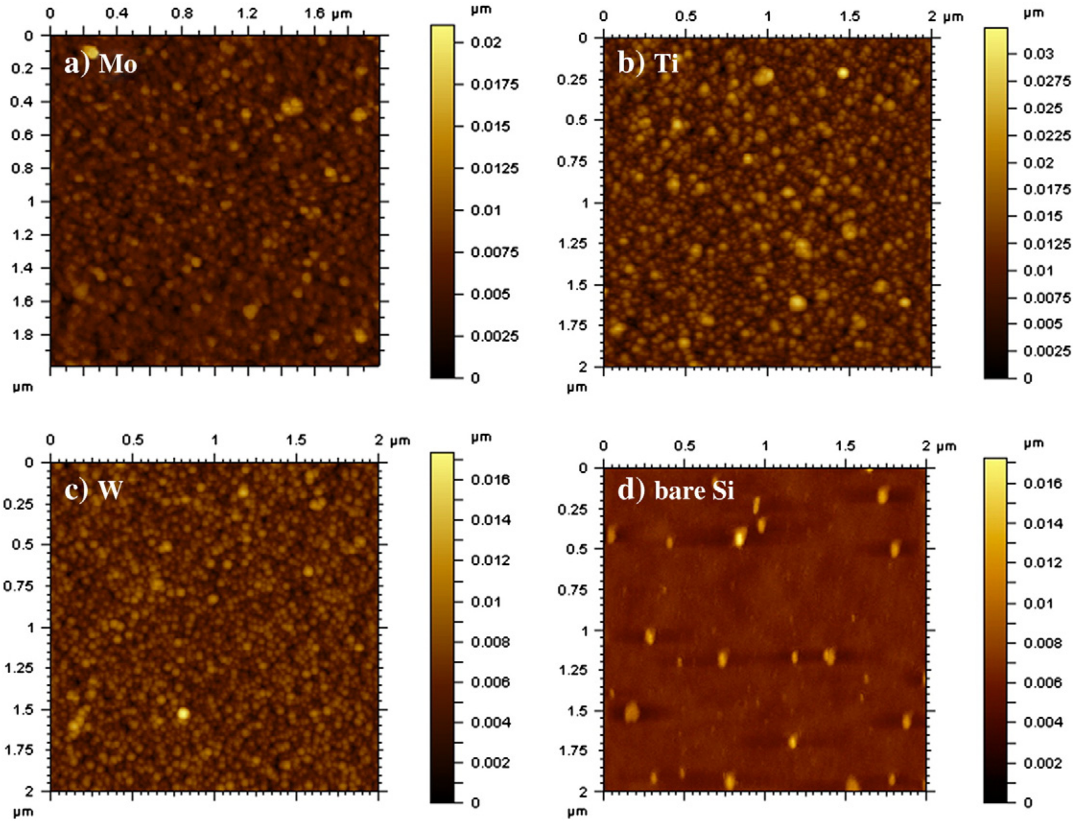

Fig. 1. AFM topographical images of three metallic layers and bare Si.