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Amorphous carbon films with MoCu dual-doping deposited by a hybrid sputtering system

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ABSTRACT

Amorphous carbon films containing a wide-range content of Mo and a small amount of Cu (MoCu:a-C films) were prepared by a hybrid sputtering system. The influences of the doping contents of MoCu on the microstructure and properties of the films were studied. The results show that the doped Cu atoms tend to dissolve in the a-C matrix while the doped Mo atoms exist as solid solution and carbide nanoparticles embedding in the a-C matrix. It is found that the size of the carbide nanoparticles shows an influence on the formation of the sp^2-C. Increasing the nanoparticle size will decrease the sp^2-C fraction and thus increase the sp^3/sp^2 in the films. The high sp^3/sp^2 and hard carbide nanoparticles contribute to the high hardness of the films. However, the hard carbide nanoparticles cause serious abrasive wear performances.

1. Introduction

Amorphous carbon (a-C) films always attract the researchers' attention due to their unique set of properties including high mechanical strength, chemical durability, biocompatibility, and wear resistance [1–4]. Thanks to these excellent properties, a-C films are very promising for a variety of technical applications such as applications in cutting tools and dies, magnetic data storage, micro-electromechanical devices, and biological implants [5–8]. However, some disadvantages, like high residual compressive stress that produced in the process of forming sp^3 bond, low thermal stability due to the metastable sp^3-C structure and intrinsic brittleness seriously limit the extended utilization of a-C films under harsh conditions [9–11]. To expand the range of practical application, a-C films are modified by doping different foreign elements. The character of the interaction between the introduced metal and the carbon matrix depends on the nature and content of the doped metal atom. Second phases will be formed and separate from the carbon matrix as the doping content exceeds a certain level. The second phase may be carbide nanoparticle or metal nanocluster which is related to the chemical nature of the doped metal. For the non-carbide forming elements, like Cu [12] and Ag [13] that do not form chemical bonds with carbon, they are incorporated into a-C films in the form of isolated metal nanoparticles. While for the carbide forming elements, like Mo [14] and W [15], they will bond with C and form hard carbide phase in the a-C matrix when they are doped into the a-C. However, both the non-carbide forming elements and carbide forming elements will dissolve in the carbon matrix when the doping contents of the metals are very low.

It is clear that the chemical state and existence form of the doped atoms will pronouncedly influence the property of the a-C films. For instance, in our previous work, we find that when the doping content is very small, the doped Cu tends to dissolve in the carbon matrix without forming any nanostructures and thus can play a role of the interstitial atoms for stress relaxation. However, as the doped Cu content is very high, Cu atoms will separate from the carbon matrix to form Cu nanoclusters, resulting in the decrease of the interstitial Cu atom number [12]. On the other hand, the carbide (e.g. MoC and WC) nanoparticles embedding in the carbon matrix can significantly improve the a-C mechanical properties [14,15]. This means that the co-doping of the metal atoms that can facilitate the formation of the carbide nanoparticles and that prefer to solubilize in carbon matrix will be one of the best methods for improving the a-C films.

Accordingly, in this paper, the non-carbide forming element Cu with a small content and carbide forming element Mo with a wide range of doping content were co-incorporated into a-C films by using a hybrid sputtering system including a DC-magnetron sputtering and a high

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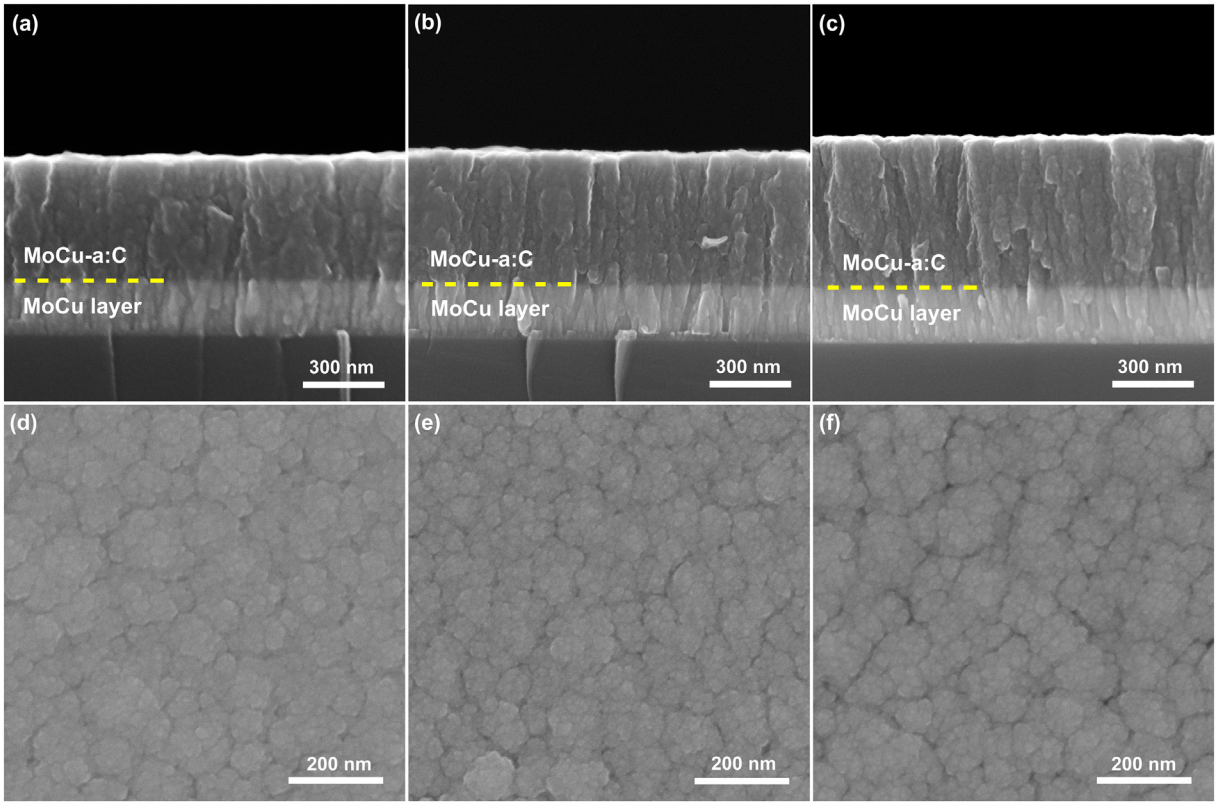

Fig. 1. SEM images of the surface topography and the corresponding cross-section morphology of the as-deposited films deposited with various sputtering powers of MoCu: (a) and (d) 10 W, (b) and (e) 30 W, and (c) and (f) 70 W.

power impulse magnetron sputtering (HIPIMS). The HIPIMS can apply high short pulsed power of low duty cycle to the target, resulting in high target power densities, which allows high plasma density and ionized rate [16]. The composition, microstructure, residual stress, mechanical properties and tribological behaviors of the films were studied as a function of the MoCu doping contents in the films. The relationships between the microstructure, internal stress, mechanical properties and tribological behaviors were discussed in detail.

2. Experimental details

A series of MoCu: a-C films were deposited on silicon (100) and steel wafers using the hybrid sputtering system consisted of the DC magnetron sputtering equipped with a MoCu alloy target (Mo/Cu = 95/5 at. %, purity 99.9%) and HIPIMS equipped with a graphite target (purity 99.9%). The distance between the target and the substrate is approximately 10 cm. The Si wafers were ultrasonically cleaned followed by in acetone and ethanol for 10 min and then dried by N_2 blow before being put into the vacuum chamber. The base pressure was evacuated to the vacuum of 5×10^{-3} Pa and the chamber was heated and the chamber temperature was maintained at 200 °C. Prior to deposition, DC glow discharge with a bias voltage of −700 V were used to etch the substrates for 10 min. Subsequently, a MoCu buffer layer with a thickness of about 200 nm was deposited on the substrates to improve the adhesion by sputtering of MoCu target (0.6 kW of pulse DC power supply, −200 V bias voltage and 60% duty ratio). Ar with a flux of 60 sccm was introduced into the chamber to maintain the deposition pressure around 0.5 Pa in the deposition process. The substrate holder rotation speed was set at 10 rpm. The average power for the HIPIMS unit was set at about 0.7 kW for the graphite sputtering. The target peak voltage and the pulse repetition frequency of the HIPIMS were about 627 V and 300 Hz, respectively, and the duty ratio was approximately 30%. The pulse DC power (60% duty ratio) of the MoCu sputtering unit was adjusted from 10–70 W to vary the MoCu sputtering contents. The bias voltage applied to the substrate was set at −100 V and the deposition time was 120 min.

Scanning electron microscope (Hitachi S-4800) was used to observe the growth morphologies of the films. The chemical composition and chemical bonds of the as-deposited films were characterized by using an X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) with Al (mono) Kα (hv = 1486.6 eV) with a step size of 1 eV. The high-resolution XPS spectra with a step size of 0.05 eV were also taken. To remove contaminants and oxide on the surface of the films, Ar^+ ion beam with energy of 2 kV was used to etch the sample surface for 5 min (The etch depth was about 10 nm). The contents of the elements in the films were calculated from the relative area ratios of the peaks in XPS spectra divided by the corresponding atomic sensitivity factors. In addition, the carbon atomic bond details of the films were measured by using the Raman spectroscopy with a 532 nm Nd:YAG laser (5 mW). More micro-structures of the films were detected by using a high-resolution transmission electron microscopy (TEM) (FEI Tecnai G2 F20S-Twin microscope) with a 200 kV acceleration voltage. The TEM specimens were prepared using mechanical polishing and precision ion polishing system (Gatan PIPS691).

The compressive residual stress of the films was calculated according to the method early published by Stoney el al. [17], where the curvature of the film/substrate composite that was determined by a laser tester. The hardness and elastic modulus of the films were measured by using a nano-indentation technique (CSM, NHT^2) with a Berkovich diamond indenter under constant load of 10 mN. The maximum indentation depths were controlled around 1/10th of the film thicknesses to eliminate the effect of the soft substrate. 15 replicate indentations were made for each sample. The tribological behaviors of the films were measured using a ball-on-plate tribometer (CSM, THT) with an Al_2O_3 ball (6 mm in diameter) as a counterpart material. The sliding tests were conducted with a rotational speed of 200 r/min under