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Study on nanocrystalline Cr_2O_3 films deposited by arc ion plating: I. composition, morphology, and microstructure analysis

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ABSTRACT

Nanocrystalline Cr_2O_3 thin films were deposited on silicon wafers with (100) orientation by arc ion plating (AIP) technique at various negative bias voltages. By virtue of X-ray diffraction analysis, scanning electron microscope, and high-resolution transmission electron microscope, the influence of substrate bias voltage on the film growth process, microstructure, and characteristics was investigated systematically, including the phase constituents, grain size, lattice constant, chemical compositions, as well as surface and cross-section morphologies. With increasing the bias voltage, the grain size and lattice constant of AIP Cr_2O_3 films first decreased slightly, and then increased gradually again. Both reached the minimum (35 nm and 13.57 Å) when the bias voltage was −100 V. However, the bias voltage had little effect on the phase constituents and chemical compositions of AIP Cr_2O_3 films. During the film growth process, the surfaces of Cr_2O_3 films were getting smoother with the negative bias voltage increase, in the meantime, their microstructures evolved from coarse columnar grains to fine columnar grains, short columnar recrystallized grains, and fine columnar grains again.

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1. Introduction

Chromium sesquioxide, Cr_2O_3, also known as chromia, is an insulating, anti-ferromagnetic ceramic with extreme physical properties (very high melting and boiling points) and is among the hardest oxide materials [1]. In thin film form, this material exhibits very attractive properties such as chemical inertness, mechanical strength, optical characteristics, high hardness and low friction coefficient, and as a result has been widely used in many fields, such as corrosion protection, wear resistance, electronics, and optics, etc. [2–6]. Although Cr_2O_3 has a bulk hardness of 9–11 GPa, the films as thin as 20 nm have been deposited with hardness up to 30 GPa, which is attributed to a high compressive stress (3–4 GPa) [7]. Again, the lowest friction coefficients are achieved with polycrystalline films [3].

It has been reported that Cr_2O_3 thin films could be deposited by various synthesis techniques, such as plasma spraying [8], spray pyrolysis [9], electrochemical deposition [10], arc ion plating [11], e-beam evaporation [12], metal-organic chemical vapor deposition [13], pulsed laser deposition [14], direct current sputtering [15], and radio frequency (RF) magnetron sputtering [16]. Among these techniques, arc ion plating is one of the most efficient physical vapor deposition (PVD) techniques due to the high kinetic energy of the ions, ionization efficiency, and deposition rate, which can produce many metal, nitride, and oxide films. Its main working principle is the use of cathode arc discharge in vacuum to deposit various films with high qualities. At the same time, a negative bias connecting to the substrate holder was used to accelerate metallic ions, which can adjust the kinetic energy of ions and improve the adhesion between film and substrate. Ji et al. [11], employing AIP technique, had investigated the influence of oxygen flow rate on the microstructure, morphology, and mechanical properties of the Cr_2O_3 films. The results showed that the thin film with less macroparticles can be obtained at high oxygen flow rate. The optimum oxygen flow rate is about 130 sccm, in this case, the hardness of Cr_2O_3 film can reach 36 GPa. Yun et al. [17] systematically investigated the effects of various oxygen additions on the microstructure, microhardness, and oxidation resistance of AIP Cr-O-N coatings. It was found that a B1-CrN phase first appeared as oxygen was incorporated into the Cr-O-N coatings. With increasing oxygen content in the coatings, the B1-CrN phase evolved into the more

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stable Cr_2O_3 phase when the oxygen content in the coating was larger than 43.0 at.%. However, few articles reported that nanocrystalline Cr_2O_3 films were deposited by AIP technique, as well as the influence of negative bias voltage on the growth characteristics of Cr_2O_3 films.

The aim of this work is to deposit high-quality nanocrystalline Cr_2O_3 thin films on silicon wafers by AIP technique. The influence of substrate bias voltage on the film growth process, microstructure, and characteristics was investigated, including the phase constituents, grain size, lattice constant, chemical compositions, as well as surface and cross-section morphologies.

2. Experimental details

2.1. Deposition of the Cr_2O_3 films

Chromium oxide films were deposited on single-crystalline Si wafers (sample size: 40×30×0.7 mm) with (100) orientation at various bias voltages by using an arc ion plating system. A direct current power supply (IDP-1010, KODIVAC Ltd., South Korea) was used to provide substrate bias voltage. The arc cathode with a diameter of 80 mm for the Cr (99.99 wt.% purity) target was at a distance of 350 mm from the rotating substrate holder. A schematic diagram of the coating system had been depicted in detail in the previous studies [17,18]. The substrates were cleaned in an ultrasonic cleaner bath by using acetone and alcohol solution for 20 min, respectively, and then were placed on the substrate holder opposing the target surface in the vacuum chamber. Prior to the Cr_2O_3 film deposition, the substrates were cleaned by Cr ion bombardment under −700 V negative bias voltage for 3 min, which would remove contaminants and ensure good adhesion of the deposited films. After that a Cr interlayer with the deposition time of 5 min was introduced to provide critical metal-to-oxide bonding and to reduce stresses. In order to avoid poisoning of the target during the oxide film deposition process, the protective gas (Ar) at a fixed flow rate was introduced into the vicinity of Cr target. The purity of argon and reactive gas (O_2) was 99.999%. The thickness of all Cr_2O_3 films in this work was kept about 3.5 μm by controlling the deposition time. Under the same conditions, the deposition rate of Cr_2O_3 films with different bias voltages had been accurately measured in advance and listed in Table 1. The detailed deposition parameters for nanocrystalline Cr_2O_3 films fabricated by arc ion plating technique are listed in Table 2.

2.2. Characterizations of the Cr_2O_3 films

The phase identifications and microstructure analysis of the Cr_2O_3 films deposited on Si wafers, were conducted using an X-ray diffractometer (XRD, D8 ADVANCE) with monochromatic Cu Kα ($\lambda = 0.154056$ nm) radiation operated at 40 kV and 40 mA. A locked couple θ-2θ mode with a 0.02° step size and a 0.2 s step time was employed. The analyzed range of diffraction angle 2θ was between 25° and 80°. An electron-probe microanalysis (EPMA, Shimadzu, EPMA 1600) was carried out to determine the chemical compositions of the Cr_2O_3 films. The surface roughness of the as-deposited Cr_2O_3 films was measured by a Stylus Profiler (SP; Alpha-Step IQ, KLA-Tencor Corporation). In the stylus profilometry measurements, the scan speed, stylus force and scan length were 50 μm/s, 0.23 mN and 2 mm, respectively. The diameter of stylus tip used in this study was 5 μm. The values of surface roughness presented in this paper are the average of five measurements. The film morphologies of cross section and surface were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) coupled with an energy dispersive X-ray spectroscopy (EDS, Oxford ISIS).

The structural information for the selected samples was obtained from the transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns, and high-resolution transmission electron microscopy (HRTEM) images. To do this, a field emission transmission electron microscope (FE-TEM, JEOL JEM-2010F) with a 200 kV accelerating voltage was used, in the meantime, it was equipped with ultra-high-resolution objective lens ($C_s = 0.5$ mm) and in-column energy filter. The latter was used to select only the elastic electrons for the HRTEM image formation. The cross-sectional TEM specimens were prepared by milling in a focused ion beam (FIB) system.

Table 1
Deposition rate of AIP Cr_2O_3 films with various bias voltages under the same conditions.

Deposition rate (μm/h)	Substrate bias voltage (V)
1.47 ± 0.15	0
1.59 ± 0.17	−25
1.86 ± 0.12	−50
2.10 ± 0.16	−100
1.72 ± 0.12	−150
1.56 ± 0.14	−200
1.28 ± 0.11	−250

Table 2
Detailed deposition parameters for nanocrystalline Cr_2O_3 films fabricated by arc ion plating technique.

Parameters	Value
Base pressure (Pa)	3.5×10^{-3}
Working pressure (Pa)	3.0×10^{-1}
Deposition temperature (°C)	300
Arc current (A)	55
DC bias voltage (V)	0, −25, −50, −100, −150, −200, −250
Ar:O_2 gas flow ratio (sccm)	40:20
Substrate rotation speed (rpm)	25
Film thickness (μm)	~3.5
Distance between the target and substrate (mm)	350

3. Results and discussion

3.1. Bias current and ion current density

Fig. 1 describes the variations of bias current with increase of the substrate bias voltage during the Cr_2O_3 film deposition process. It can be observed that the bias current increased approximately linearly with increasing the negative bias voltage. This is a well known effect that is related to an increase of dissipated bias power on the substrate. That is to say there were more charged ions directed to the substrate in each moment at higher negative bias voltage, which resulted in larger bias current, even if the "re-sputtering effect" under ion bombardment also failed to affect the above trends. In an arc ion plating process, the ionization rate can reach about 80–90% [19]. The main species devoting to the bias current are the positive charged ions

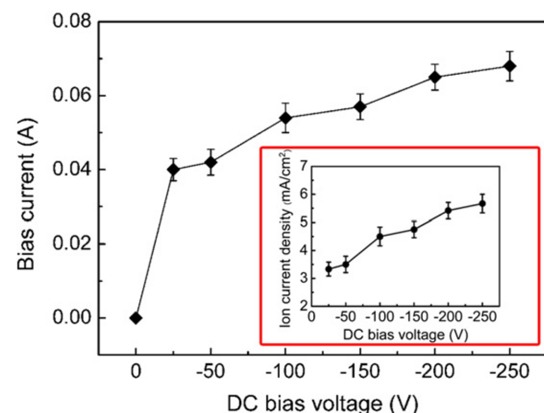

Fig. 1. Variations of bias current and approximately calculated ion current density with increasing the substrate bias voltage during the Cr_2O_3 film deposition process.

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