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Epitaxial (100)-oriented Mo/V superlattice grown on MgO(100) by dcMS and HiPIMS

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ABSTRACT

Epitaxial (100)-oriented Mo/V superlattices have been grown by High Power Impulse Magnetron Sputtering (HiPIMS) and dc Magnetron Sputtering (dcMS) on single-crystalline MgO(100) substrates at growth temperatures ranging from 30 °C to 600 °C. Superlattice bilayer period of Mo/V around 12/12 monolayers and 15 repeat periods was studied. This study aims to investigate the effect of the HiPIMS process on reducing the growth temperature of Mo/V superlattices using the high energy ionized Mo, V species in the HiPIMS plasma. In one case, the Mo layer was only grown with the HiPIMS process and V layer grown using the dcMS process while in another both layers were grown with the HiPIMS process. The as-deposited films were characterized by X-ray reflection and diffraction techniques. The dcMS process was found to give superior superlattice growth at high growth temperatures while a mixed Mo HiPIMS and V dcMS process gives better result at lower growth temperatures (300 °C). Room temperature growth reveals that neither the mixed Mo HiPIMS and V dcMS process nor the pure HiPIMS for both materials can produce better result compared to the pure dcMS process, which gives a relatively better result.

1. Introduction

Various types of bcc superlattices grown on MgO(100) substrates have been investigated for the last two decades using magnetron sputtering methods. The best known superlattices are based on Fe/V and Mo/V repeat structures but other structures such as Nb/Ta, Mo/Nb and Nb/W exist. Fe/V superlattices can be grown with good quality at temperature around 200 °C to 300 °C while Mo/V requires a temperature of 700 °C to obtain similar quality [1–4]. Lower mobility of the molybdenum atoms at the Mo surface during the growth is the reason for the higher growth temperature [5]. Applications of Mo/V superlattice coating system are few. It has been used in basic research area studying phenomena in superconductivity, intermixing and hydrogen uptake [6–8]. In this paper Mo/V is used to study fundamental relative merits of conventional dc magnetron sputtering (dcMS) over high power impulse magnetron sputtering (HiPIMS) techniques. HiPIMS is an ionized physical vapor deposition (IPVD) technique resulting in better growth than dcMS because of the higher degree of ionization and energy of the sputtered vapor [10,11]. Its benefits include increased film density [12,13] and surface roughness modification [14,15]. HiPIMS growth of metallic superlattice has not been reported but compound superlattices such as CrN/NbN [16] and CrAlYN/CrN [17] have been grown previously. Paulitsch et al. also reported the superior mechanical and tribological properties of a CrN/TiN superlattice grown by hybrid HiPIMS/dcMS process that resulted low friction coefficients in the range of diamond-like-carbon coatings in ambient conditions [18].

In this study we investigate the effect of the HiPIMS process on reducing the growth temperature of Mo/V superlattices using the high-energy ionized Mo, V species in the HiPIMS plasma. In one case, the Mo layer was only grown with the HiPIMS process and the V layer grown by the dcMS process while in another case both layers were grown with the HiPIMS process. Mo has lattice parameter of 0.315 nm and V 0.302 nm, which givesa considerable lattice mismatch which is relaxed with a misfit dislocation generation when individual layers are growing. MgO(100) substrate has a lattice parameter of 0.421 nm which provides a good epitaxial base where the bcc unit cell is rotated 45° with respect to the substrate surface axis. The MgO epitaxial lattice then has a lattice parameter of 0.298 nm which is closer to the V lattice parameter. Lower mismatch and improved superlattice crystalline quality is therefore possible by reducing the ratio between Mo (thickness X ML) and V (thickness Y ML) [9]. Here we decided to grow a symmetric superlattice inorder to keep both layers under similar misfit strain during growth and keep the superlattice period close to 12/12 monolayers, well under the known stability limit of Mo/V superlattice growth, 16/16 monolayers [2].

2. Experimental apparatus and methods

Deposition of the Mo/V superlattice samples was performed in a custom-built magnetron sputtering chamber [19] with a base pressure of 3.5×10^{-6} Pa. Mo and V targets of 99.995% purity and 3 in. (75 mm) in diameter were used, in a planar balanced magnetron configuration. The sputtering gas was argon of 99.999% purity. For the HiPIMS growth, the argon flow rate was $q_{Ar} = 40$ sccm. A throttle valve was used to set a total growth pressure of 0.7 Pa. In the dcMS growth, the argon flow

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rate was $q_{Ar} = 20$ sccm and the throttle valve maintained a total growth pressure of 0.4 Pa.

The dcMS power was generated by an Advanced Energy MDX500 power supply. For HiPIMS, the power was supplied by a SPIK1000A pulse unit (Melec GmbH) operating in a unipolar negative mode at a constant voltage, which in turn was charged by a dc power supply (ADL GS30). The discharge current and voltage were monitored using a combined current transformer and a voltage divider unit (Melec GmbH). The data was acquired with a LabVIEW software. The pulse repetition frequency was 75 Hz and the pulse length was 200 μs. The films were grown in three different processes: 1) a normal dcMS, 2) a mixed Mo target HiPIMS process and a V target dcMS process and finally 3) a Mo and V combined HiPIMS process with both targets connected to the same power supply.

The dcMS process was operated in a constant power mode applying 50 W to both Mo and V targets with the applied voltages 390 V and 320 V, respectively. In the mixed Mo HiPIMS and V dcMS process, the average power was 90 W, pulse voltage 1000 V and for the V target, dcMS power was 50 W. The combined Mo/V target process was run at a total power of 100 W and pulse voltage of 450 V. The target voltage and target current waveforms are shown in Fig. 1. The peak power density was in the range of 0.180–0.250 kW/cm^2 for all samples.

The substrate was located 145 mm from the target surface facing each target at an angle of 22.5°. MgO(100) substrates with 1 mm thickness and size of 1 cm by 0.5 cm were used. A circular plate heater 1.5 in. (38 mm) in diameter placed behind the substrate holder controlled the substrate temperature during the growth. It was separated from the substrate holder by a 2 mm gap. No bias was applied to the substrate holder which was kept floating during the growth. The substrate holder design is described in more detail elsewhere by Arnalds et al. [19]. The MgO substrates from Crystal GmbH Germany showed domain structures 0.2° wide in normal scan with local domains peak widths of 0.025° in normal and rocking directions. The substrates were heated to 620 °C for 10 min. The growth temperatures were 30 °C, 300 °C, 400 °C and 600 °C, giving 12 different superlattice samples. Deposition times for each target material were either calibrated or estimated in order to get superlattice repeat length as close to 12/12 monolayers as possible. Growth times of 79 s, 79 s, and 127 s were used for the V layers in the pure dcMS, the mixed dcMS–HiPIMS, and the pure HiPIMS processes, respectively. For the Mo layers, the growth times were 31 s, 57 s, and 86 s in turn for the pure dcMS, the mixed dcMS–HiPMIS, and the pure HiPIMS processes, respectively. All samples were grown with 15 bilayer repetitions. The total thicknesses were in the range of 45–60 nm giving good visible thickness fringes in the X-ray reflectivity (XRR) scans.

A PANalytical's X'pert diffractometer was used to perform X-ray diffractometry (XRD) (Cu K_α, wavelength 0.1541 nm). A hybrid monochromator/mirror was mounted on the incident side and a 0.27° collimator on the diffracted side. A line focus was used with a beam width of approximately 1 mm. The film density, film thickness and surface roughness were obtained from low-angle XRR measurements with an angular resolution of 0.001°. Parratt formalism [20] for reflectivity was used for fitting the XRR data with accuracy of 0.1 nm for the thickness analysis. The dcMS process showed growth rates of 0.05 and 0.02 nm/s for Mo and V, respectively. In the mixed process the Mo HiPIMS growth rate was 0.03 nm/s. In the third process, the pure HiPIMS mode, growth rates of 0.02 and 0.01 nm/s were obtained for Mo and V. All growth rates were obtained at 600 °C. The superlattice repeat length was in most cases 3.2 nm with variation of ±0.2 nm due to uncertainty in determining the growth rate in advance for different growth temperatures and determining the magnetron shutter opening times.

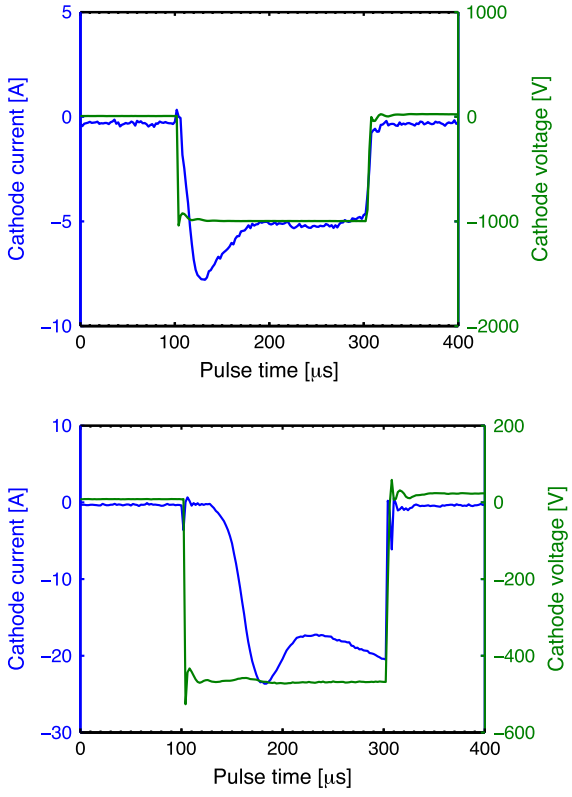

Fig. 1. Waveforms of the HiPIMS cathode current and voltage. Shown are process 2) mixed Mo HiPIMS process (shutter open) and V dcMS (shutter closed). Process 3) Mo HiPIMS shutter open V HiPIMS shutter closed. The other shutter configuration showed similar waveform shape.

3. Results and discussion

Generally, the growth rate depends on ion flux density, sputtering yield and film density for any sputtering process [21]. The lower growth rate observed when using the HiPIMS process over the dcMS process for growing materials is well-known and mostly due to the return effect [22,10,13].

In this work, results for the three different growth temperatures of the three processes are visualised by the results of the XRR measurements as shown in Fig. 2. The measured curves were fitted using XRR software in all cases to get thicknesses and growth rates of the different materials. In all cases bulk density values of Mo or V were able to fit the measured XRR curves around the critical angle of reflection.

The reference sample used was the 600 °C dcMS sample which shows an excellent XRR curve with well-defined thickness and superlattice patterns. The sample reflectogram could be fitted with the XRR software using ideal superlattice structure with roughness values less than one monolayer. The mixed process sample grown at 600 °C did not show the same quality. Its higher order superlattice peaks were broader, which indicates layer thickness fluctuations, higher roughness value ±1.5 ML and disappearance of reflectivity fringes. The pure HiPIMS process sample grown at 600 °C had a similar quality but showed the reduced intensity in the reflectivity fringes at higher scattering angles.

When lowering the growth temperature to 400 °C, the structural quality of the layers reduced somewhat. The dcMS sample was still of good quality but the interface roughness increased to ±2 ML. The mixed process sample grown at 400 °C also showed lower quality. Its higher order superlattice peak was broader indicating layer thickness fluctuations and higher roughness value of ±3 ML. The pure HiPIMS process sample grown at 400 °C only showed one superlattice peak which indicates a still higher roughness.

Reducing the growth temperature to 300 °C, the trend reverses, the dcMS process shows much reduced structural quality of the superlattice layers. The mixed process sample grown at 300 °C showed the highest