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On the film density using high power impulse magnetron sputtering

Mattias Samuelsson [a,b,*], Daniel Lundin [a], Jens Jensen [c], Michael A. Raadu [d], Jon Tomas Gudmundsson [e,f], Ulf Helmersson [a]

[a] Plasma & Coatings Physics Division, IFM-Materials Physics, Linköping University, SE-581 83 Linköping, Sweden
[b] Impact Coatings, Westmansgatan 29, SE-582 16 Linköping, Sweden
[c] Thin Film Physics Division, IFM-Materials Physics, Linköping University, SE-581 83 Linköping, Sweden
[d] Division of Space and Plasma Physics, School of Electrical Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[e] Science Institute, University of Iceland, Dunhaga 3, IS-107 Reykjavik, Iceland
[f] Department of Electrical and Computer Engineering, University of Iceland, Hjardarhaga 2-6, IS-107, Reykjavik, Iceland

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ABSTRACT

The influence on thin film density using high power impulse magnetron sputtering (HiPIMS) has been investigated for eight different target materials (Al, Ti, Cr, Cu, Zr, Ag, Ta, and Pt). The density values as well as deposition rates have been compared to results obtained from thin films grown by direct current magnetron sputtering (DCMS) under the same experimental conditions. Overall, it was found that the HiPIMS deposited coatings were approximately 5–15% denser compared to the DCMS deposited coatings. This could be attributed to the increased metal ion bombardment commonly seen in HiPIMS discharges, which also was verified using a global plasma model to assess the degree of ionization of sputtered metal. One key feature is that the momentum transfer between the growing film and the incoming metal ions is very efficient due to the equal mass of film and bombarding species, leading to a less pronounced columnar microstructure. As expected the deposition rates were found to be lower for HiPIMS compared to DCMS. For several materials this decrease is not as pronounced as previously reported in the literature, which is shown in the case of Ta, Pt, and Ag with $rate_{HiPIMS}/rate_{DCMS}$ ~ 70–85%, while still achieving denser coatings.

1. Introduction

High power impulse magnetron sputtering (HiPIMS) is a promising technique for improving magnetron sputtering today being used in many industrial processes for thin film deposition [1]. The HiPIMS discharge generates large quantities of highly energetic ions [2] due to very high pulse power densities with, in some cases, a directed flux of charged species [3]. The transport of these energetic particles is not fully understood, but it is clear that they have a dramatic effect on thin film growth, such as densification and improved adhesion [4].

Previous studies on HIPIMS have shown that for some cases the increase in thin film density can be as much as 30% [5], whereas other reports claim slightly more than 10% [6] compared with conventional techniques such as direct current magnetron sputtering (DCMS) or mid-frequency asymmetric bipolar pulsed magnetron sputtering. In a recent study on CrN deposition, Alami et al. measure a density increase of about 6% when depositing with HiPIMS compared to DCMS, although the stoichiometry of the deposited films was not reported [7]. These values depend not only on process conditions and system configuration, but also heavily on source material, making it difficult to draw any conclusions regarding trends in film densification between separate studies. This stresses the need for the present study of single element metal sputtering processes, keeping the complexity and variation in process conditions at a minimum. By doing so, it may be possible to determine whether or not there is an overall trend in change of film density when using HiPIMS as compared to DCMS. It is of essence to investigate this property, since the film density is an important parameter for many types of coatings, such as mass-diffusion barriers, thermal barriers as well as for corrosion protection and wear resistance.

There are indications in the literature on film densification mechanisms that may give valid information to explain the observed behaviour for the HiPIMS films density increase. From transmission electron microscopy studies by Petrov et al. [8] it is known that an increase in the ion flux greatly reduces intracolumnar as well as intercolumnar porosity, where it is suggested that the incoming ions collisionally enhance the surface mobility. Molecular dynamics simulations of multilayer thin film growth when varying the ion/metal flux ratio also show that the film roughness is reduced for an increased ion flux [9]. This has also been experimentally confirmed by Eriksson et al. [10], and they conclude that ion assistance leading to a higher ion/metal flux ratio results in an increased ad-atom mobility and a smoothening effect. They also point out that for ion energies in the range 20–30 eV the coatings become denser. In a dedicated

* Corresponding author. Department of Physics, Chemistry & Biology, Linköping University, SE-581 83, Linköping, Sweden. Tel.: 46 13 282712; fax: 46 13 137568.
E-mail address: matsa757@ifm.liu.se (M. Samuelsson).

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HiPIMS study by Alami et al. [4], the importance of a highly metallic ion deposition flux for film densification is also stressed. From ion energy measurements in HiPIMS discharges it has been found that the average metal ion energy is around 20 eV, whereas the argon gas ions show much lower average energies (< 10 eV or less), without using any substrate bias [2,3].

Furthermore, a high ionized flux fraction has been demonstrated in several independent works on HiPIMS. The fraction of ionized metal has been shown to reach above 90% for Ti [11]. For Cu the measured ionized flux fraction was estimated to approximately 70% by Kouznetsov et al. [12] and Cu^+ was measured to be almost 92% of the total ion flux to the substrate as reported by Vlcek et al. [13]. For conventional magnetron sputtering discharges, the ionized flux fraction is of the order of a few percent [14]. It is therefore suggested that the discharge conditions for HiPIMS are such that both a high relative flux of metal ions as well as the desired ion energy are present.

Also reported for HiPIMS processes is the lower deposition rate as compared to DCMS values [1,15,16] under similar conditions. There are likely a number of reasons for this behaviour such as back-attraction of ionized sputtered material [15], the magnetic arrangement and anomalous transport of charged species in HiPIMS discharges, which is more thoroughly discussed in a previous publication [3]. In general, it is clear that the transport of the sputtered material is greatly affected by electric and magnetic fields when a large fraction is ionized as in the case of HiPIMS. This can also be seen when comparing the deposition rates for different magnetic field configurations (see for example references [17,18]). Konstantinidis et al. also show that the relative deposition rate in the case of Ti changes dramatically from 20% to 70% when decreasing the pulse length [19] and thereby affecting the discharge characteristics such as level of self sputtering taking place as well as neutral gas heating followed by gas depletion and change of plasma conductivity [20]. Furthermore, in a work by Helmersson et al. [21] it was shown that the reduction in relative deposition rate was particularly pronounced for metals with a low self-sputtering yield.

In this study eight different metallic materials (Al, Ti, Cr, Cu, Zr, Ag, Ta, and Pt), all relevant for many deposition processes, have been chosen for a more detailed study of the film density and deposition rates when using HiPIMS. No compound materials were used in order to minimize the complexity of the system. The density values were measured and compared with results from thin films grown under equivalent conditions using DCMS in addition to tabulated bulk values. The impurity content and its effect on the density have also been analyzed. The overall results were compared to a global plasma model providing insights on the ionization of the sputtered metal ions, which subsequently are transported to the substrate during growth.

2. Methods and materials

2.1. Experimental details

The thin films investigated in this work were deposited in a high vacuum deposition system. Here, a planar circular $\Phi = 0.076$ m magnetron (Gencoa Ltd) equipped with different commercially available metal targets (Al, Ti, Cr, Cu, Zr, Ag, Ta, and Pt), having a thickness of 0.003175 m (1/8 in.), with the exception of Ta, being 0.00635 m (1/4 in.) thick. The target purities varied depending on material. Since commercial targets were used, the purity was in all cases above 99%, which was verified by the RBS and ERDA analyses. The magnetron was mounted in a cylindrical vacuum chamber (height 0.30 m, diameter 0.42 m) pumped with a turbo-molecular pump to a background pressure of about 7×10^{-5} Pa, after which Ar, with a minimum purity of 99.9997%, was leaked into the chamber. The discharge pressure was 0.67 Pa unless otherwise stated. Si substrates were placed on a static substrate holder at a distance of 0.065 m from the target surface. The substrate holder was grounded. All depositions were performed at ambient temperature, and at least four samples were deposited for each process condition. In this investigation the average power was kept constant at 125 W for both deposition methods, except in the case of Pt and Ta where the average power was slightly lower due to voltage limitations of the charging power supply. In the case of HiPIMS, unipolar voltage pulses were applied to the magnetron by a pulsing unit (SPIK 1000A, Melec GmbH) charged by a direct current (DC) power supply (Pinnacle, Advanced Energy) delivering constant voltage pulses of controlled length. The specific voltage and current characteristics varied depending on target materials, but typical values of ~880 V and ~30 A were used generating approximately 100 μs discharge pulses at 100 Hz. Since the power pulse characteristics were fed into the global plasma model described below, it is here worth mentioning that little difference in the appearance of the resulting power pulse characteristics between the different target materials was seen.

For DCMS, a DC power supply (MDX 1 K, Advanced Energy) was connected to the magnetron set to deliver a constant power of 125 W.

The density (ρ) of the deposited thin films was obtained by measuring the areal atomic density (N_S) by Rutherford backscattering spectrometry (RBS) and the film thickness (t) independently. For a single element film the density is then calculated as $\rho = (N_S/t) \times (M/N_A)$ [22], where M is the atomic mass and N_A is Avogadro's number. This method has previously been used by Wang et al. to successfully evaluate thin film densities [23]. In order to measure the film thickness a scanning electron microscope (SEM, LEO 1550 Gemini) as well as a stylus profilometer (Vecco Dektak 6 M) were employed. Both the aforementioned methods were used on all films in determining the film thickness mean value. The accuracy of the SEM were in this work a few tens of nm and the thickness values were averaged over a 1 cm wide cross section of the film in order to minimize any errors. In the case of the profilometer it has a maximum vertical resolution of 10 nm. To facilitate reliable RBS analysis, all film thicknesses were between 350 and 500 nm.

The RBS measurements were performed at the tandem accelerator of Uppsala University, using a 2.0 MeV $^4He^+$ beam with a backscattering angle of 172°. The incident angle was 6° with respect to the surface normal (to avoid channelling effects in the substrate). The obtained spectra were evaluated using the SIMNRA 6.04 code [24]. For RBS, the dominant contribution to the uncertainty is associated with the uncertainty in stopping cross section for the respective elements [22]. The error is typically 3–5%, and in the present study 5% was chosen for all elements. In order not to underestimate the error for the density calculations, a minimum and maximum value for the density was calculated using the standard error for the RBS results and the extreme values in the film thickness determination. The error bars for the density values thus serves as an upper limit of the actual error. Furthermore, time-of-flight elastic recoil detection analysis (ToF-ERDA) [25] was employed to estimate the level of impurities hidden in the RBS spectra. As primary projectile 40 MeV $^{127}I^{9+}$ ions were used, the incident angle was 22.5° and the detector was placed at a recoil scattering angle of 45°. The information gained from the ToF-ERDA measurements was fed back to the SIMNRA evaluation in order to better reflect the composition of the measured samples.

2.2. Plasma modelling

In this work, a new, time-dependent (zero-dimensional) plasma model based on works by Ashida et al. [26], Hopwood [27], and Gudmundsson [28] was employed to simulate ionization and gas dynamics during the HiPIMS discharge. The model operates by solving the coupled differential equations, essentially similar to those given in detail by Gudmundsson [28]. However, in the present model the production and loss of ions, electrons, and neutral species is assumed