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Composition of the sputter deposited W–Ti thin films

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ABSTRACT

Tungsten–titanium (W–Ti) thin film was deposited by dc Ar^+ sputtering of W(70 at.%)–Ti(30 at.%) target. The thin film composition, determined by X-ray photoelectron spectroscopy (XPS) depth profiling, is $W_{(0.77\pm0.07)}Ti_{(0.08\pm0.03)}O_{(0.15\pm0.03)}$. The presence of oxygen in the deposit is due to the rather poor vacuum conditions during the deposition, while significant deficiency of Ti, as compared to the sputtering target composition cannot be explained straightforwardly. Monte Carlo simulations of both, transport of sputtered particles from target to the substrate through the background gas (SRIM 2003 program) and thin film sputtering during the XPS depth profiling (program TRIDYN_FZR) are presented. The simulations show that the particle transport through the background gas is mainly responsible for the Ti depletion: the estimated composition of the thin film is $W_{0.61}Ti_{0.16}O_{0.23}$. Additional apparent Ti depletion occurs due to the preferential sputtering during the thin film composition analysis. The simulation of the sputtering process show that the surface concentration measured by XPS should be about $W_{0.74}Ti_{0.11}O_{0.15}$. The discrepancy between the estimated surface composition and the actual experimental result is in the range of the experimental error.

1. Introduction

Tungsten–titanium (W–Ti) thin films have many significant properties from the technological point of view such as low electrical resistance, thermal stability, oxidation resistance, chemical inertness and good adhesion towards metal contact and the substrate [1–3]. They are widely used in the microelectronic industry as diffusion barrier layers between Al [4–6], Cu [6] or Ag [7] contact layers and a silicon substrate. Diffusion properties of W–Ti thin films depend strongly on the concentration of Ti [8]. Sputter deposition is particularly useful in the case of depositing multicomponent systems since it provides (in contrast to vapor deposition for instance) very good control of the thin film composition. In a first approximation, the sputter deposited thin film and the corresponding target should have the same composition [9,10]. However, it was observed by several groups that Ti concentration in W–Ti thin films is significantly lower than that of the target (cf. [3,6,11,12] for instance).

In general, the transport of sputtered atoms from a target to a substrate is influenced by the collisions with gas atoms [11]. The main parameter which determines the transport of sputtered particles through background gas is *pD*, where, *p* is the pressure of the background gas and *D* the distance between the target and the substrate. Three regimes can be identified: (a) at low values of this parameter the transport is *ballistic*: the collisions with gas atoms can be neglected and the thin film composition corresponds to that of the target; (b) at high values of *pD* the transport is *diffusive*, i.e., it is characterized by simple gas diffusion and again, thin film composition corresponds to that of a target (the diffusion of sputtered atoms is proportional to the gradient of the concentration and size and mass of sputtered atoms have no influence); (c) between these two is *intermediate* regime, characterized by intermediate values of *pD*. In this case the lighter sputtered atoms are usually scattered more rapidly from the gas atoms than the heavier, i.e., the energy losses of lighter atoms are enhanced. Consequently, the lighter element has greater stopping in the background gas, which contributes to its depletion in the deposit. The ranges of *pD* which correspond to these regimes depend on both, background gas and sputtered particles. W–Ti sputter deposition with argon as a background gas is a typical system for which depletion of Ti can be expected in the intermediate

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regime. Titanium depletion in W–Ti thin films was qualitatively explained in this manner by some authors [3,11]. In the case of some deposition techniques, it is found that Ti deficiency can be also due to the deposit resputtering by the ions from plasma [8,12].

Measurement of the thin film composition is not a trivial task either. Generally, it is performed by different surface sensitive techniques. However, thin film composition determined in this way is incorrect if surface segregation and/or contamination take place. In order to overcome this problem, depth profiling of a deposit composition using ion sputtering followed by surface analysis is frequently performed [13–15]. If the thin film composition is determined by the analysis of sputtered particles, as in the case of secondary ion mass spectroscopy, the obtained result will correspond to the composition of the original thin film interior. However, if it is determined using some of the surface sensitive techniques (such as Auger electron spectroscopy or X-ray photoelectron spectroscopy (XPS), to mention the most popular), the additional problem might arise due to the preferential sputtering. As the lighter atoms are usually preferentially sputtered [16], measurement of W–Ti thin film composition using XPS depth profiling could contribute to additional apparent Ti depletion in the deposit.

We have deposited W–Ti thin films by dc sputtering with Ar as a background gas. As the thin film surface composition significantly differs from that of the target interior [17], the thin film composition was determined using XPS depth profiling. Our aim in this work is to quantitatively explain the discrepancy of the measured W–Ti thin film composition with respect to that of the W–Ti target. This is done by Monte Carlo simulations of both, particle transport through the background gas (program SRIM) and the surface composition change due to the preferential sputtering during the depth profiling (program TRIDYN_FZR). From this data we can estimate the real thin film composition which is, as already stated, of great importance to the diffusion properties of W–Ti thin films.

2. Experimental

Thin film of W–Ti was deposited in the Balzers Sputtron II system. Schematic of the deposition system is presented in Fig. 1. Argon ions are formed in the ionization chamber and extracted to the deposition chamber by the extraction voltage of about 50 V. Plasma is confined inside the cylindrical steel shield by the magnetic field. Therefore, it interacts with target but not with substrate. Argon ions are accelerated by the electric field in the vicinity of the target: the chamber and the shield are on earth potential while the target is on high negative potential V_t. The angle between the target surface and the direction defined by the centers of the target and the substrate holder is 30°. The substrate holder has a shape of a plate with the diameter $d = 20$ cm. The distance between the centers of the target and the substrate holder is $D = 30$ cm. Substrate holder rotates around two axes, presented in Fig. 1. The system is evacuated by 450 l/s turbo-molecular pump.

The target composition used for the thin film deposition was W:Ti (70:30 at.%), which was produced by sintering of W and Ti powders in the appropriate weight ratio (90% W, 10% Ti). The substrate was *n*Si (1 0 0) wafer, cleaned in HF solution and in deionized water before mounting into the deposition chamber. The base pressure was about 1×10^{-3} Pa, while the working pressure of Ar gas was 1×10^{-1} Pa. The substrate surface was cleaned by bias sputtering for about 2 min at $I = 50$ mA and $V = -1$ kV. The ion current on the target and the target potential during the deposition process were $I = 0.7$ A and $V_t = -1$ kV, respectively. The pressure difference in the deposition chamber before (after) and during the deposition was less then 10%. The sputtering deposition was performed at room temperature and the deposition rate was approximately 0.155 nm/s. The thickness of deposited W–Ti thin films is 105 nm, measured by Talystep.

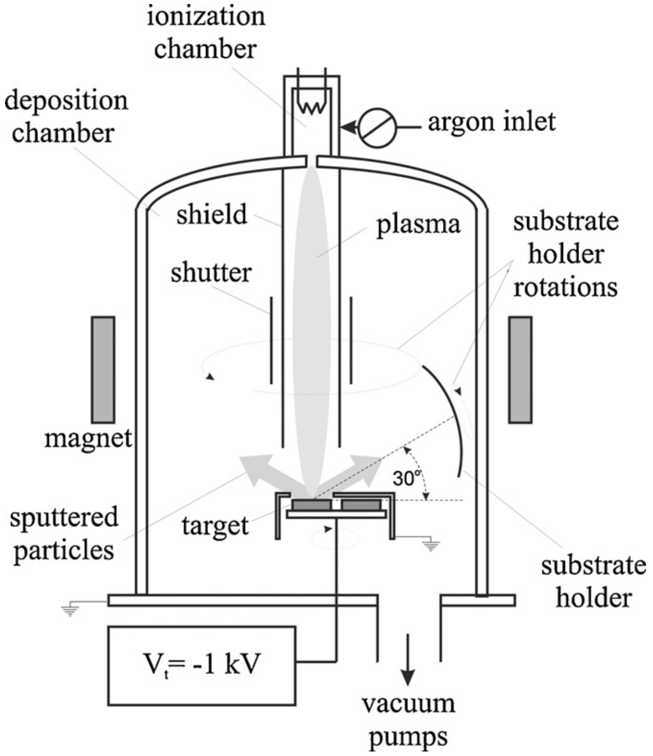

Fig. 1. Schematic of the deposition system.

The XPS analysis of the W–Ti thin film was performed by the PHI XPS-TFA spectrometer. The Al Kα X-ray beam was used for the analysis of as-received surface and during the XPS depth profiling. The spectra of Ti 2p, W 4f and O 1s were taken at resolutions of about 0.9 eV. The depth profile of the W–Ti film was obtained by the ion bombardment of sample surface by 3 keV Ar^+ ions. A take-off angle of photoelectrons was 45° with respect to the sample surface. The sample rotation at angular velocity of 1 revolution/min was applied during the depth profiling in order to avoid roughness development due to the ion beam bombardment. The mean sputtering rate was calculated from the thickness of the W–Ti film, measured by Talystep profilometer and the time needed to reach W–Ti/Si interface during the XPS depth profiling. The obtained value is 2.14 nm/min. Concentrations of elements were calculated from the peak areas using the sensitivity factors provided by the instrument manufacturer, i.e. 0.733 for O 1s, 3.863 for W 4f and 2.077 for Ti 2p and 0.157 for C 1s.

3. Monte Carlo simulations

In order to make the modeling of the deposition process significantly simpler, several assumptions were adopted: (a) sputtered particles are transported through Ar gas (the presence of W and Ti atoms in the background gas is neglected), (b) background gas density distribution is constant in time and space, (c) there are no interactions of the deposit with charged particles, (d) the sticking coefficient of W and Ti atoms is equal and (e) plasma does not ‘see’ the substrate, which could cause resputtering of the deposited material. The *pD* parameter in our case is about 3 Pa cm. Since the lower limit for the diffusive regime for W–Ti system is about 15 Pa cm [11], the transport regime in our experiments was intermediate or ballistic. Therefore, deposition