

Energetic Considerations for Sputter Deposition Processes

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Abstract—Sputter deposition processes, especially for sputtering from metal targets, are well investigated. For practical reasons, i.e. for industrial processes, energetic considerations for sputter deposition are useful in order to optimize the sputtering process. In particular, for substrates at floating conditions it is required to obtain energetic conditions during film growth that enables sufficient dense metal films of good quality. The influence of ion energies, energy density and momentum transfer is thus examined both for sputtering at the target as well as during film growth. Different regimes dominated by ion energy, energy density and momentum transfer were identified by using different plasma sources and by varying power input, pressure and bias voltage.

Keywords—Energy density, film growth, momentum transfer, sputtering.

I. INTRODUCTION

SPUTTER deposition processes are nowadays well understood [1], [2]. Seah recently gave an accurate semi-empirical equation for sputtering yields [3]. The so-called single-knock and linear cascade regimes are well covered by this equation [4]. Nevertheless, it is still under discussion, whether simple approaches based on energetic considerations such as ion energies, energy density and momentum transfer are helpful or even misleading [5]–[7], which also involves HiPIMS [8] and plasma polymerization [9]. This discussion is related to threshold energies for sputter deposition processes as well as to the influence of the way of energy input on different film properties. Therefore, we examine the regimes for different energy-related parameters in sputter deposition processes.

The ion energies incident on a surface are related to the voltage drop between the plasma (where the ions originate) and the surface. Without collisions by travelling through the sheath separating the plasma and the surface, a simple relation holds for the mean ion energies:

$$E_{mean} = eV_{sh}, \quad (1)$$

where e is the unit charge and V_{sh} the sheath voltage (voltage drop in front of the target or the substrate). Due to collisions in the plasma sheath, this energy is reduced to (in good approximation)

$$E_{mean} = eV_{sh} \left(1 + c \frac{L}{\lambda}\right)^{-1} \quad (2)$$

where $c = m_n / (m_i + m_n)$, i.e. $c = 0.5$ for ions (with mass m_i) colliding in their parent gas (with mass m_n), L is the sheath thickness and λ the mean free path [9]–[11].

The energy density during film growth is given by

$$\varepsilon_{surf} = E_{mean} \frac{\Gamma_i}{\Gamma_{dep}} \quad (3)$$

with the ion flux Γ_i incident on the surface and the flux of depositing particles Γ_{dep} which correlates to the atomic deposition rate when etching or back sputtering processes are absent [12]. The ion flux originates from the plasma with plasma density n_i and thus depends on collisions within the presheath of length D due to the acceleration to the Bohm velocity v_B (Bohm criterion to leave the bulk plasma) [13]:

$$\Gamma_i = 0.86 v_B n_i \left(3 + \frac{D}{\lambda}\right)^{-0.5} \quad (4)$$

The momentum transfer during film growth is finally given by

$$\pi_{surf} = 2\sqrt{2m_i E_{mean}} \frac{\Gamma_i}{\Gamma_{dep}} \quad (5)$$

Different regimes strongly governed by ion energies, energy density or momentum transfer can be identified both for sputtering and film growth.

II. EXPERIMENTAL

The sputter deposition processes were performed by DC (unbalanced) magnetron sputtering and RF sputtering in a strongly asymmetric set-up by varying pressure p and power input W . For magnetron sputtering a magnetron from AJA International Inc. (“Stiletto” type ST20-O-C-M) was used with a silver target of 2 inch size. Si wafers were mounted on floating conditions with a typical distance of 6.5 cm from the target. The substrate position can be varied to change the energetic conditions during film growth. Furthermore, an RF electrode can be used to apply an additional substrate bias (also placed 6.5cm from the target). For RF (13.56 MHz capacitively coupled) sputtering a plasma reactor with a slab

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geometry of width 5cm was used. The driven silver electrode was mounted on top inside the reactor facing the lower grounded electrode, where the substrates (Si wafers) were placed. The area ratio of Ag to ground electrode was roughly

5:100 enabling a high bias voltage at the Ag electrode. Ar was used as sputtering gas throughout all experiments (Table I).

TABLE I
USED PARAMETERS FOR THE SPUTTER DEPOSITION OF SILVER IN AR

Sputtering mode	Pressure [Pa]	Power input [W]	V_T [V]	V_S [V]	L_T [mm]	L_S [mm]	$n_{e,max}$ [10^{16} m^{-3}]
DC magnetron	2	255	410	15	1.0	0.3	13
DC magnetron	2	50	320	15	1.0	0.3	3.0
DC magnetron	80	255	325	7.5	0.4	0.6	20
RF asymmetric	10	50	315	55	7	6	1.2

V_T and V_S are the voltage drop in front of the target and substrate, and L_T and L_S the sheath thickness in front of the target and substrate.

Deposition rates as well as sputtering rates were measured by weighing using a microbalance (Mettler Toledo XS204, resolution of 0.1mg).

Electron densities n_e (which equal the plasma density n_0 for electropositive gases such as Ar) were measured by MW interferometry (JE Plasma Consult MWI 2650). The maximum electron density $n_{e,max}$ was measured at a distance of 1cm from the target. As mean free path λ for Ar charge exchange collisions 7mm·Pa was taken [14]. Roughness (average roughness R_a) and grain size were measured by AFM (Easy Scan 2) using images with an area of $1 \times 1 \mu\text{m}^2$.

III. RESULTS AND DISCUSSION

A. Sputtering at the Target

For a sputtering process to occur, the energy input must at least exceed the surface binding energy, which is in the range of 1-8 eV [15]. Assuming a surplus of energy required for an atom to leave the surface and not just undergo surface diffusion, the threshold in ion (or particle) energies incident on the target for sputtering by single-knock events is still small (<10 eV) [16]. Suitable sputtering conditions, however, occur above approximately 25 eV of incident particle energy. With increasing ion energies the energy can be spread more uniform in the target surface. The resulting increase in sputtering yield becomes proportional to the ion energy (Fig. 1).

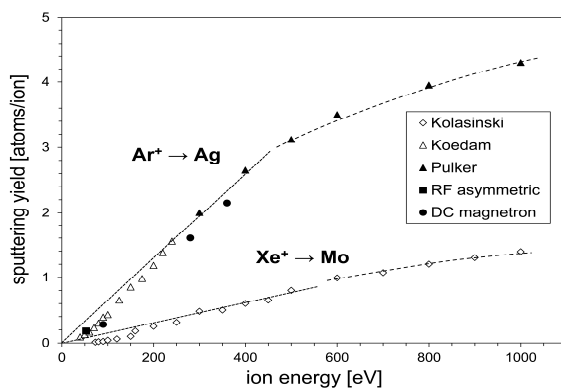


Fig. 1 Sputtering yield vs. ion energy for sputtering of Ag targets (in Ar) and Mo (in Xe). Data were taken from literature and own data has been added

For this regime, for example, an energy density of ~ 150 eV per released (sputtered) atom in Ar^+ (250-500 eV) sputtering of silver (Ag) or ~ 650 eV per released atom in Xe^+ (300-600 eV) sputtering of molybdenum (Mo) can be calculated from literature data as observed from [17]–[19]. That means that e.g. 150 or 650 eV dissipates in the target by multiple collisions before one atom (with a few eV) is released. Only when this specific energy density is exceeded, the energy input is sufficient that collision cascades via momentum transfer dominate the sputtering process. Hence, the sputtering yield follows the square root of the ion energies for energies higher than 500 eV in Ar^+ on Ag and 600 eV in Xe^+ on Mo, respectively. This momentum transfer can be calculated to $\sim 210 (\text{eVamu})^{0.5}$ per released atom for Ar^+ on Ag and $\sim 650 (\text{eVamu})^{0.5}$ for Xe^+ on Mo.

The sputtering yields of Ag sputtering in Ar obtained for own experiments agree well with the literature data. Low sputtering yields observed for high pressure (80Pa in magnetron sputtering and 10 Pa in RF sputtering) support the view of the importance of ion energy for the single-knock processes, where the energy density is much higher than 150 eV per released atom. This effect is also pronounced for low energy ions in Mo sputtering in Xe.

B. Sputter Deposition

Next, the energetic conditions during film growth are examined. For magnetron sputtering at floating potential, the width of sheath L and presheath D are a few Debye length (see Table I). At low pressure (2Pa) it can thus be considered as collisionless. The energy density thus depends on the plasma density close to the position of the substrate (Fig. 2), while mean ion energy E_{mean} and atomic deposition rate Γ_{dep} remain constant by moving the sample in front of the target.

Power variation and sample position can thus be used to adjust the energetic conditions during film growth at floating conditions. It is interesting to note that lower power densities yield higher energy densities due to the strongly reduced deposition rate (6.3 nm min^{-1} compared to 48.6 nm min^{-1} at higher power input). The surface mobility is reduced due to lower energy densities with increasing deposition rate [20]. Energy densities in the order of 10 eV per deposited atom are required to obtain a preferred orientation of microcrystals, i.e. to enable densification and crystallization by enhanced surface mobility [21]. A transition from zone 1 (needle-like growth

with voids and low film quality) to zone T (denser structure with enhanced film quality) within the structure zone diagram can thus be achieved. Small grain sizes and smooth surfaces ($R_a = 1.1\text{nm}$) have been obtained. At enhanced energy densities collision cascades are enabled that further densify the film during growth governed by the momentum transfer [5], [9]. The induced compressive stresses, however, strongly depend on the value of the mean ion energy incident on the substrate, as well [5], [22].

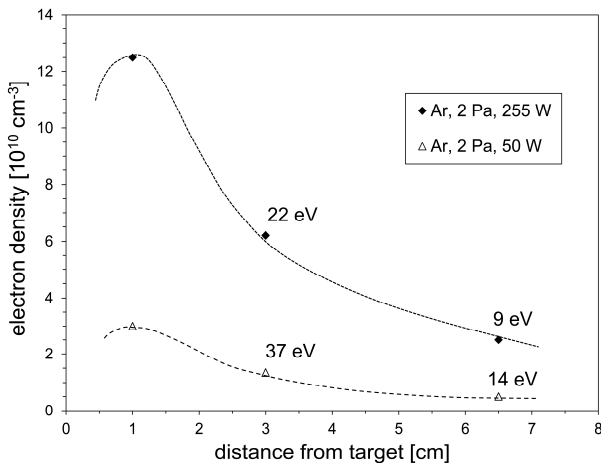


Fig. 2 Electron density vs. distance from target for magnetron sputtering of Ag in Ar at a pressure of 2 Pa and varying power input. The line was drawn to guide the eyes. In addition, the energy densities are given in eV per deposited Ag atom

Optimized energetic conditions during metal film growth at floating potential are for example important for the metallization of yarn that is guided through the plasma zone in a reel-to-reel process. Thus excellent adhesion and electrical conductivity can be obtained for nanoscaled Ag films enabling conductive fibers for smart textiles [23]–[25].

At elevated pressure the decrease of ion energy and ion flux incident on the substrate with the distance from the target becomes more pronounced [26]. Nevertheless, the RF sputtering process (without magnetron) also enables an energy density of around 10 eV per deposited Ag atom at the grounded electrode. Thus comparable film qualities are obtained as for the magnetron sputtering process at a distance of the floating substrate of 6.5 cm from the target. The deposition rate, however, is much lower (0.7nm min^{-1} compared to 48.6 and 6.3 for 2 Pa, 255 W and 50 W, respectively). Even for the high pressure of 80 Pa (DC magnetron, 255 W), an energy density of around 10 eV per deposited Ag atom can be observed due to the low deposition rate of 0.8nm min^{-1} . The Ag films, however, become much rougher ($R_a \approx 10\text{nm}$) forming larger grains and showing a reduced film quality, which can be ascribed to the much lower ion energies (below 2 eV, i.e. below the surface binding energy of Ag of 3.3 eV) incident on the substrate. Hence, there might be also a threshold for ion energies with respect to surface diffusion processes during film growth similar as

observed during sputtering.

Introducing an additional electrode into the sputter deposition process, a (negative) bias voltage might be applied to the substrate, if it is a flat, thin substrate (in case it is insulating) that can be brought in close contact with this electrode (such as Si wafers). The additional bias voltage increases the voltage drop in front of the substrate by leaving the plasma parameters unaffected in the approximation of first order [27]. Hence, the mean ion energies incident on the substrate can be enhanced and thus the energy density and momentum transfer during film growth. With increasing ion energies, however, also the sputtering yield increases resulting in a superposition of deposition and backsputtering (Fig. 3).

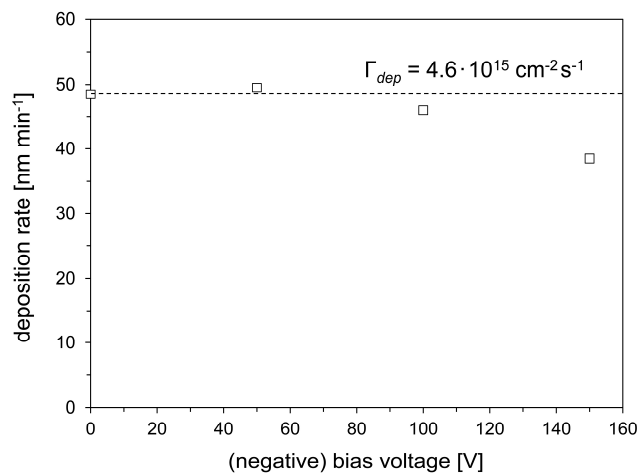


Fig. 3 Deposition rate vs. applied substrate bias voltage in Ag sputter deposition (magnetron sputtering, 2 Pa, 255 W). At all conditions a constant flux of depositing Ag atoms can be assumed

Typically, at a bias above 100 V (at low pressures) the net deposition rate is found to decrease [28], [29]. Applying a bias voltage it has to be considered that the sheath thickness in front of the substrate grows so that collisions become more frequent (superposition of floating sheath and RF sheath) [27], [30]. The mean ion energy thus increases less than the bias voltage. Furthermore, it should be regarded that also the ion flux might be increased by an additional bias voltage [31].

Note that for the calculation of the energy density according to (3) the incident flux of depositing atoms has to be taken into account instead of the (measured) net deposition rate. This also holds for plasma polymerization where etching processes occur, e.g. for the deposition of hard coatings, since the removed atoms also take up energy. Requiring a threshold in the order of the bond energies, the momentum transferred to the growing film yields densification of the coating [9]. Increasing ion energies, however, also result in increasing intrinsic stresses [6], [22]. Therefore, the ion energies reveal an optimum range for a certain film deposition, while an increase in ion flux, on the other hand, mainly enables the control of film quality as well as an increase in deposition rate [7], [32].

IV. CONCLUSION

Sputtering from a target in the range up to about a few keV typically shows different regimes according to minimum ion energy, a minimum energy density and momentum transfer. In the first regime, sufficient energy has to be present in a single-knock process to overcome the surface binding energy. In the second single-knock regime, the energy spreads more uniform yielding a constant energy density during sputtering. At higher energies finally, collision cascades are enabled and the sputtering yield follows the momentum transfer to the target.

Similar regimes can also be observed during film growth. Minimum particle energy is required to enable surface mobility, which is further enhanced by increasing energy density and momentum transfer enabling densification. Considering (3) and (5) there are three ways to increase ϵ_{surf} or π_{surf} by increasing the mean ion energy, by increasing the ion flux or by lowering the deposition rate. The latter is often undesirable for industrial processes. While a minimum ion energy seems to be required (in the order of bond energies), increasing ion energies support the formation of intrinsic stresses. Thus, the most suitable way to enhance surface mobility is via the ion flux. Therefore, the plasma density (electron density) should be enhanced which might also be carried out by additional ionization sources.

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