

Observation of Self-Sputtering in Energetic Condensation of Metal Ions

Andre Anders
Lawrence Berkeley National Laboratory

June 2004

Observation of Self-Sputtering in Energetic Condensation of Metal Ions

André Anders

Lawrence Berkeley National Laboratory, University of California,

1 Cyclotron Road, Berkeley, California 94720-8223

Abstract

The condensation of energetic metal ions on a surface may cause self-sputtering even in the absence of substrate bias. Charge-state-averaged self-sputtering yields were determined for both zirconium and gold ions generated by a cathodic vacuum arc. Films were deposited on differently biased substrates exposed to streaming Zr and Au vacuum arc plasma. The self-sputtering yields for both metals were estimated to be about 0.05 in the absence of bias, and exceeding 0.5 when bias reached –50 V. These surprisingly high values can be reconciled with binary collision theory and molecular dynamics calculations taking high the kinetic and potential energy of vacuum arc ions into account.

Energetic condensation can be defined as a deposition process where condensing (film-forming) species have hyperthermal energies. Energetic condensation has attracted attention in the framework of ion plating,¹ the synthesis of diamond-like carbon films,² and semiconductor metallization by ionized Physical Vapor Deposition.³ At hyperthermal energies, film-forming ions or atoms are inserted under the surface (subplantation). Film growth by subplantation² has been associated with desirable properties such as good film adhesion, reduction of roughness, and high density and hardness.

A practical approach to implementing energetic condensation is to utilize streaming metal plasma from a cathodic arc plasma source. The cathode is the feedstock material, and phase transformations from solid metal to plasma occur at micron-size, non-stationary cathode spots.⁴ Accelerated by extreme pressure gradients and electron-ion coupling, ions reach a high velocity, which is supersonic with respect to the ion sound velocity.^{5,6} The average final velocity will be designated with v_{i0} , and the corresponding average “natural” kinetic energy of cathodic arc ions is $E_{i0} = m_i v_{i0}^2 / 2$.

Negative substrate bias provides an additional boost to positive ions before they impact the substrate surface. The ion charge state, Q , which is often +2 or +3 for many cathode materials,⁷ is a multiplier for the kinetic energy gain determined by the sheath voltage, V_s , and thus the total kinetic energy can be written as

$$E_{i,kin} = E_{i0} + QeV_s, \quad (1)$$

where e is the elementary charge.

The high energy in the condensation process from cathodic arc plasmas suggests that subplantation may be accompanied by self-sputtering. Sticking probability and self-sputtering yield will affect the net growth rate, texture, and morphology of a growing

film. The sticking probability is defined as the probability that the incident ion remains bound to the solid, and the self-sputtering yield is defined as the number of surface atoms ejected per incident ion. Little or no information is available on self-sputtering yields for the case of condensing cathodic vacuum arc plasmas without or at low bias voltage.

In the present work, the relevance of self-sputtering for condensing cathodic vacuum arc ions is investigated at various bias voltages. Certainly, the effect will depend on the specifics of the material considered. One would suspect that self-sputtering is especially important for heavy ions and materials of small surface binding energy.

The experimental approach was to measure the difference between expected film thickness, based on measurements of the current of ions condensing on a substrate of known area, and actual film thickness, measured by profilometry. The self-sputtering yield can be determined from

$$\gamma_i = \frac{N_i - N_f}{N_i} \quad (2)$$

where N_i is the number of ions incident on the substrate during the deposition process, and N_f is the number of atoms found in the film after deposition. Equation (2) has the shortcoming that it does not account for sputtering of the substrate, which will occur at the very beginning of the deposition process, and it does not allow for $\gamma_i > 1$. Therefore, when $\gamma_i \approx 1$ is found, the actual yield may exceed unity and substrate material may have been sputtered.

The substrate current (I_s), is composed of ion current (I_i) and secondary electron current (I_{se}),

$$I_s = I_i + I_{se} \equiv I_i (1 + \gamma_{se}), \quad (3)$$

and

$$N_i = \int \frac{I_s(t)}{Q(t)e(1+\gamma_{se})} dt. \quad (4)$$

The actual experiment was done with pulsed plasmas, and therefore the expression

$$N_i \approx \frac{1}{\overline{Q_p} e(1+\gamma_{se})} \sum \int I_s dt \quad (5)$$

was used. The summation is over the number of pulses, and the integral is over the duration of one arc pulse. Because the mean ion charge state was not simultaneously measured, previous results⁸ for $\overline{Q_p} = \int Q(t) dt / \tau_p$ were used instead.

The secondary electron emission at can be ascribed to two mechanisms: potential emission (PE) and kinetic emission (KE). PE is characterized by an Auger-type process in which at least two conduction band electrons are involved, one neutralizing the arriving ion into the ground state, and the other being excited into the continuum above the filled band.⁹ The yield by PE is generally small, about 0.1, and therefore can be neglected. KE is a process where the ion transfers kinetic energy to electrons in the metal to eject them above the surface barrier into the vacuum. KE has an energy threshold and it is safe to neglect KE for the energy range in the present experiment.¹⁰ Hence, Eq.(5) can be simplified to

$$N_i \approx \frac{1}{\overline{Q_p} e} \sum \int I_s dt. \quad (6)$$

The number of atoms in the film was determined by measuring the film thickness, h ,

$$N_f = \frac{A \rho_f}{m_i} h, \quad (7)$$

where the constant factor contains the known substrate area, A , the film mass density, ρ_f , and the ion mass, m_i .

The experimental setup is shown in Fig. 1. A cathodic arc source of the minigun type was used. It consists of a cathode rod of 6.25 mm diameter and an annular anode of 2.5 cm inner diameter. Cathode and anode were separated by a ceramic tube that had a conducting coating used for arc triggering. The arc discharge was repetitively pulsed, with 3 pulses per second. Each arc discharge was fed by a pulse-forming network of 0.4 Ω impedance. The charging voltage was 350 V, the nominal current in the flat portion of the pulse was 780 A, and each pulse had a duration of 0.5 ms. The vacuum base pressure was 10^{-4} Pa; no working gas was involved at any time.

Eleven independently biased substrates were positioned 50 cm from the cathodic arc plasma source. Each substrate consisted of a stainless steel disk, 2.5 cm in diameter, on which a piece of polished Si wafer was glued using conducting silver paste. Such large distance was chosen to ensure that the plasma plume could expand for relatively uniform coating of the samples.

A stiff voltage divider and capacitor system provided stable bias voltages unless arcing occurred. Arcing was only a problem for the highest bias (-100 V and -90 V) and only at the beginning of the experiment. Bias voltage was monitored using a 10:1 voltage divider. The whole experiment was repeated several times, with 8000 arc pulses per deposition.

The current to the substrate with the highest bias was monitored using a broadband current transformer (Pearson 110, 0.1 V/A). The substrate current curve was integrated using the advanced features of a digital storage scope (Tektronix TDS744).

Using Eq.(6), the number of ions that arrived at the sample was determined by counting pulses and recording $\int I_s dt$. The thickness of each film was measured by profilometry (Dektak IIA). The films were rough, and film thickness was determined excluding peaks that were obviously caused by macroparticles.

Fig. 2 shows the result of thickness measurements as a function of bias voltage. One can immediately see that biasing causes a large effect. The film thickness decreased monotonously as the bias increased from zero to approximately -50 V. The lines inserted in Fig. 2 indicate this decrease, followed by very thin coating of nearly constant thickness at higher bias.

Additional observations should be mentioned. Firstly, in the case of gold, the effect was immediately visible. The sample at ground potential showed the characteristic gold color, which gradually disappeared on samples of higher bias. Almost no film was discernable on samples of bias exceeding -50 V. Secondly, there was noticeable gold coating on parts and components that did not have a line of sight with the plasma source, indicating that scattering in the plasma or sputtering from a surface must have occurred.

Using Eq.(2), the thickness data of Fig. 2 can be converted to self-sputtering yields (Fig. 3).

Molecular dynamics,^{11,12} binary collision theory,^{13,14} and kinetic Monte-Carlo-molecular dynamics calculations¹⁵ have been used to model the energetic interaction of hyperthermal atoms and ions with solids. For normal incidence, the sticking coefficients were determined to be unity for all materials,¹² and the self-sputtering yields at 100 eV were 0.2 for Al, 0.3 for Ni, and 0.5 for Cu. Although direct comparison with current observations is not possible, these simulations give approximately the same results and

tendencies. One should keep in mind that the total energy of most cathodic-arc Zr and Au ions exceeds 100 eV even at zero bias, taking into account not only kinetic but also potential energy.¹⁶

Sources of error need to be discussed. Above all, it should be emphasized that cathodic arcs involve non-stationary processes, and large fluctuations are seen on all data. Therefore, all results are to be understood in terms of averages.

The self-sputter yields obtained for bias exceeding -50 V should be taken with caution because substrate sputtering plays a significant role, contrary to the assumption of Eq.(2). The actual self-sputter yields will be higher, and one should only conclude that γ_i exceeds 0.5. A future, improved experiment could start with pre-fabricated film samples.

The influence of macroparticles on measured film thickness was minimized by disregarding all peaks in the film profile. To evaluate the remaining error, one needs to consider their effect on substrate current and film thickness. Macroparticles have a very small charge-to-mass ratio, and it is reasonable to neglect their electric current. Macroparticles are incorporated in the film, and hence if they did not exist, the film would have been thinner. Therefore, the actual self-sputtering yields are larger than what was measured with macroparticles, and the here-determined self-sputtering yields represent lower limits.

Another possible error is the deposition of neutrals coming from the cathode spot area. Similar arguments as with macroparticle apply, and observed yields must again be considered as lower limits.

Re-deposition of self-sputtered atoms may also affect the observed yields. Sputtered atoms may interact with the streaming plasma and some may return to the substrate. Re-deposition makes the observed self-sputtering yields to be lower limits.

Film density was assumed to be close the material's bulk density. If the real film density was less, the actual number of atoms in the film would be less for the measured film thickness, and therefore the self-sputtering yield would be even larger than what was determined.

The emission of secondary electrons is electrically equivalent to arrival of ions, and therefore the observed sputtering yields would be overestimated. As mentioned above, only PE can contribute under the present conditions. PE does not depend on the kinetic energy (i.e., bias) therefore the effect at different bias voltages cannot be caused by secondary electrons.

In summary, the self-sputtering yields for cathodic-arc Zr and Au were found to be about 0.05 in the absence of bias, and exceed 0.5 when the bias voltage was greater than -50 V. Self-sputtering leads to the presence of neutrals in cathodic arc plasmas. Implications on the evolution of ion charge-state distribution and coatings will be considered in future work. The findings are not limited to cathodic arc plasmas but applicable to all deposition processes where high degree of ionization and high kinetic energy of condensing species is involved, such as in pulsed laser deposition.

Helpful comments by J. Rosén and S. Lim are gratefully acknowledged. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Figure Captions

FIG. 1 Schematic of the experimental setup: A cathodic arc source produced a plasma streaming toward a set of 11 substrates, biased between 0 and -100 V in steps of 10 V. The substrates were arranged in a circle of 12 cm diameter. Schematic is not to scale, not all samples are shown.

FIG. 2 Result of thickness measurements as a function of bias voltage; thickness is normalized to value at zero bias; the absolute thickness was 125 nm and 50 nm for Zr and Au films, respectively. The error bars indicate the error determined by repeating thickness measurements several times.

FIG. 3 Data of Fig.2 presented as self-sputtering yield versus bias. The error bars indicate the uncertainty of the determination, including errors of parameters h , Q , and

γ_{se} .

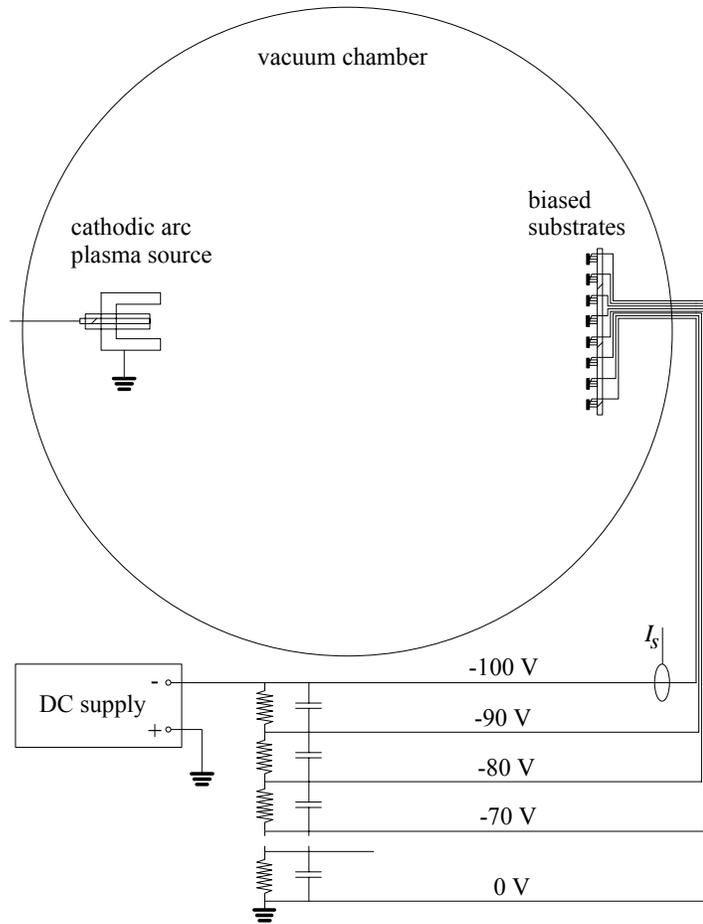


FIG. 1

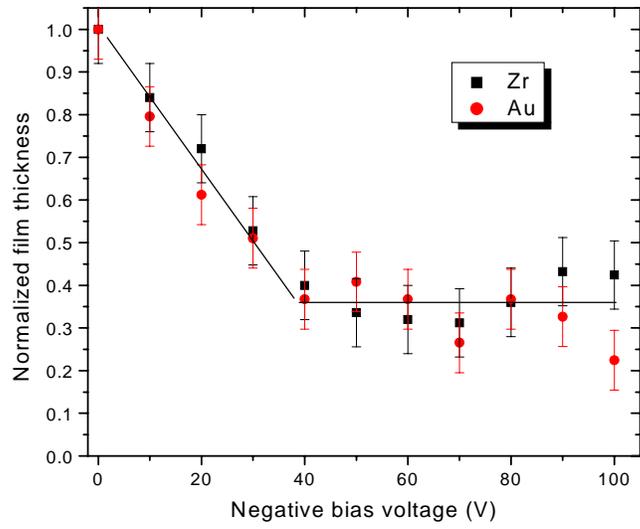


FIG. 2

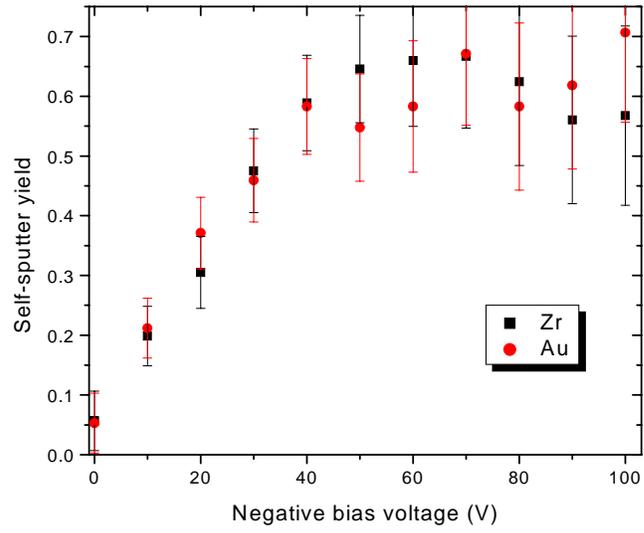


FIG. 3

- 1 D. M. Mattox, J. Vac. Sci. Technol. **10**, 47 (1973).
- 2 S. Uhlmann, T. Fraunheim, and Y. Lifshitz, Phys. Rev. Lett. **81**, 641 (1998).
- 3 S. R. Rossnagel and J. Hopwood, J. Vac. Sci. Technol. B **12**, 449 (1994).
- 4 B. Jüttner, J. Phys. D: Appl. Phys. **34**, R103 (2001).
- 5 C. Wieckert, Phys. Fluids **30**, 1810 (1987).
- 6 E. Byon and A. Anders, J. Appl. Phys. **93**, 1899 (2003).
- 7 A. Anders, Phys. Rev. E **55**, 969 (1997).
- 8 A. Anders, IEEE Trans. Plasma Sci. **29**, 393 (2001).
- 9 H. D. Hagstrum, Phys. Rev. **96**, 325-335 (1953).
- 10 G. Laktis, F. Aumayr, M. Heim, and H. Winter, Phys. Rev. A **42**, 5780 (1990).
- 11 J. D. Kress, D. E. Hanson, A. F. Voter, C. L. Liu, X. Y. Liu, and D. G. Coronell,
J. Vac. Sci. Technol. A **17**, 2819 (1999).
- 12 D. E. Hanson, B. C. Stephens, C. Saravanan, and J. D. Kress, J. Vac. Sci.
Technol. A **19**, 820-825 (2001).
- 13 W. Eckstein, *Computer Simulation of Ion-Solid Interactions* (Springer-Verlag,
Berlin, 1991).
- 14 M. Hou and W. Eckstein, J. Appl. Phys. **71**, 3975-3980 (1992).
- 15 J. M. Pomeroy, J. Jacobsen, C. C. Hill, B. H. Cooper, and J. P. Sethna, Phys. Rev.
B **66**, 235412 (2002).
- 16 A. Anders, Appl. Phys. Lett. **80**, 1100 (2002).