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Energy transfer into the growing film during sputter deposition: An investigation by calorimetric measurements and Monte Carlo simulations

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The power density at the substrate during sputter deposition was measured by a calorimetric method. In combination with measurements of the atomic deposition rate, the total amount of the energy input per incorporated atom was determined. The measured values range from 18 eV for aluminum to about 1000 eV maximum per atom for carbon. There is, for all elements investigated, a general trend for a linear increase of the energy per atom with increasing sputtering argon pressure over the range from 0.2 to 7 Pa. The energy per atom decreases with increasing power of the sputtering discharge. The application of a negative bias to the substrate reduces the total energy per atom to the values measured at low pressure of 0.4 Pa or below. The total energy flux in the low pressure range (0.4 Pa or less) can be well described by contributions due to plasma irradiation, the heat of condensation of the deposited atoms, their kinetic energy, and the kinetic energy of the reflected argon neutrals. The latter two components are *a priori* calculated by TRIM.SP Monte Carlo simulations. There is good agreement between the *a priori* calculated and the measured values. The combination of experimental and theoretical data result in empirical rules for the energies of the sputtered and reflected species, which allow an estimate of the energy input during sputter deposition for every elemental target material in the low pressure range. In a first approximation, the energy per incorporated atom is proportional to the ratio between target atomic mass and sputtering yield. © *1999 American Vacuum Society.* [S0734-2101(99)05405-6]

I. INTRODUCTION

Over the past 3 decades, magnetron sputtering (MSP) has been established as one of the most important tools in thin film deposition technology (see for example Ref. 1). There is a large variety of applications of the MSP technique, as for example hard and protective coatings, metallic interconnects in microelectronics or thin film solar cells and optical and decorative layers.[1] The growth of sputtered films leading to the formation of special types of microstructure is known to be strongly affected by the sputtering argon pressure.[1,2] In recent years, new or improved thin film materials have become widely used. It is found that sputter deposition of some of these films results in ''strange'' effects as, for example, the formation or turnover of texture or a special crystal structure as observed in titanium nitride,[3] molybdenum,[4] zinc oxide[5] or boron nitride.[6] These effects are often connected to the appearance of lateral inhomogeneities of other film properties over the substrate area. It is assumed that all these effects result from variations in the energetic bombardment of the growing film. However, there is rather small knowledge about the energy input into the growing film during sputter deposition as a function of the target material and the process parameters. Twenty years ago, Thornton[7] performed a pioneering work studying the total energy input into the growing film by a calorimetric method. The results of this work are discussed in terms of a quantitative model. From the present point of view, there is a variety of open questions regarding the results in the literature.[7] These concern the role of the discharge power and pressure on the energy flux. Thornton[7] reported on a pressure-independent energy per atom in the range from 0.1 to 1.3 Pa. In addition, the contribution of reflected argon neutrals to the energy input was not investigated quantitatively because of the lack of experimental or theoretical data. The role of reflected argon neutrals is of special interest, as argon bombardment can influence the chemical composition, crystallite size and the microscopic properties of thin films as demonstrated for Mo by Ensinger.[8] Argon bombardment is also essential for the deposition of ''zero-stress'' films.[9] The aim of the present work is the reexamination and improvement of the calorimetric measurements performed by Thornton. The experimental results are discussed by means of transport of ions in matter—sputtering (TRIM.SP) Monte Carlo simulations. The reader of the present work should be given a tool to estimate the total energy input into the growing film and the contributions of incorporated sputter atoms and reflected neutrals.

II. EXPERIMENTAL SETUP

For this investigation, two types of magnetron sputtering equipment were used. With the exception of carbon deposi-

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tion, dc sputtering was applied. The magnetron sources used are all manufactured by von-Ardenne Anlagentechnik. The target to substrate distance was $d_{ST}=8$ cm in every case. Germanium and carbon films were deposited by dc or 13.56 MHz rf sputtering, respectively, in an LA 440S commercial sputtering apparatus equipped with 125 mm diam magnetrons (for details see the previous work[10]). The other deposition apparatus is computer-controlled multichamber deposition equipment designed for the deposition of metal/semiconductor multilayers, which is described in detail in Refs. 4 and 11. Two chambers contain PPS-90UV magnetrons with 90 mm diam targets of silicon or metal (Al, Mo, W) targets, respectively. With the exception of the single crystalline Si targets and the glassy carbon target, all targets used are polycrystalline.

For the films prepared, the deposition rate was determined by measuring the films' thickness and density via x-ray reflectometry (see Ref. 4 for experimental details) and the deposition time. The x-ray measurements also gave additional information about the film properties (besides density, surface roughness, crystallite size, etc.). It was found[12] that for sputtering a variety of elemental targets in argon atmosphere, the pressure-dependent atomic deposition rate Φ_{at} is well described by the Keller–Simmons formula:[13]

$$\Phi_{at}=\Phi_0\frac{(pd)_0}{pd_{ST}}\left[1-\exp-\frac{pd_{ST}}{(pd)_0}\right]. \quad (1)$$

Here Φ_0 is the zero-pressure flux at the substrate and $(pd)_0$ is the characteristic pressure-distance product (PDP) which is element specific.[12] In a first approximation and neglecting gas density reduction effects, it can be assumed to be proportional to the product of target atomic mass, the energy of sputtered atoms and their thermal mean free path in argon.[12]

The measurements of the energy input during sputter deposition were performed applying the calorimetric method after Thornton.[7] For the single-chamber apparatus, the heat flux was measured using a molybdenum dummy substrate the size of 25×23 mm^2, the mass of 667 mg and defined heat capacity. Temperature control was performed using a 0.25 mm diam Ni–CrNiAl coaxial thermocouple attached with silver paste to the substrate. Measurements were performed by a computer-controlled voltmeter Fluke 8842. For the multichamber apparatus, the substrate heating was measured by means of a 15×15 mm^2, 0.5 mm thick Al substrate. Temperature measurements were performed by a PT 100 thermoresistor, which was electrically connected by 50 μm diam gold wires. It was operated at a voltage of 0.2 V. By means of the self-heating of the thermoresistor (at a voltage of 2 V), the heat capacity of the whole probe was determined to be 0.835 J/K. Using the gradient method after Thornton,[7] the heat loss due to conduction via the wires or the thermocouple, respectively, and due to irradiation, can be determined. The incoming power density at the substrate during deposition I_{tot} is then deduced from the effective heating of the substrate per unit area. Normalizing the power density to the atomic deposition rate results in the total energy input per incorporated atom $\langle E_t\rangle$

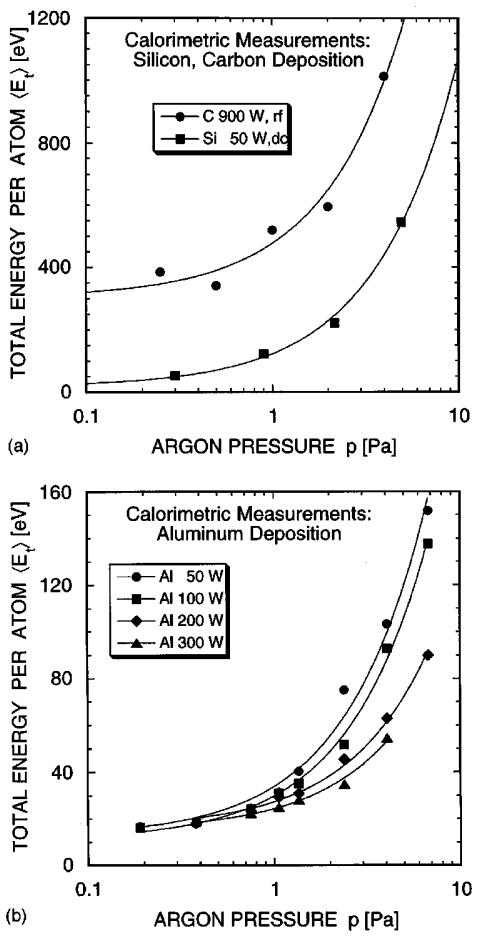

FIG. 1. Total energy input per atom as a function of argon pressure for (a) silicon and carbon, (b) aluminum. The data were taken at different sputtering powers, which are given in the legend. The solid lines are linear fit curves.

$$\langle E_t\rangle=I_{tot}/\Phi_{at}. \quad (2)$$

The simulation of the sputter process was performed using the (TRIM.SP) Monte Carlo program.[14] The principle of the program is to calculate collision cascades generated by an argon projectile penetrating the target material. The model is based on the binary collision approach (for more details, the reader is referred to Ref. 15). For each target voltage 5×10^5 sputtering events were simulated on an IBM workstation. This calculation typically took 3 h. (Note that the target voltage in V is assumed identical to the ion energy in eV—see, for example Refs. 16 and 17). The targets were assumed amorphous and perpendicular incidence of the projectiles was chosen.

III. RESULTS: CALORIMETRIC MEASUREMENTS

Figure 1(a) shows the measured energy flux for carbon and silicon. With increasing argon pressure there is an increase of the total energy input per atom up to maximum values of 1030 and 540 eV for C and Si, respectively. For the case of Al [Fig. 1(b)] the energy input per atom reaches a maximum of 152 eV. It can be seen from Fig. 1(b) that the

TABLE I. Parameter of the linear fit curves $\langle E_t \rangle = c_0 + c_1 p$, which are shown in Figs. 1(a)–3(a), describing the functional dependence of the total energy flux per atom deposited $\langle E_t \rangle$ on pressure p for different elements and sputtering powers investigated.

Element	Power (W)	c_0 (eV)	c_0 (eV/Pa)
C	900	302.89	172.59
Al	50	12.43	21.37
Al	100	10.78	18.95
Al	200	16.09	11.18
Al	300	14.89	9.43
Si	50	17.56	105.08
Ge	50	24.46	16.40
Ge	500	21.04	4.14
Mo	20	77.39	5.16
Mo	50	64.35	6.86
Mo	100	58.07	4.23
Mo	200	50.60	2.98
W	20	152.88	44.86
W	100	136.67	1.41

increase of energy input is also power dependent with the highest values obtained for minimum power. With decreasing pressure, the curves taken for different power converge into identical values, which amount to 18.6 ± 0.5 eV at 0.4 Pa argon pressure. A decrease of the pressure to 0.2 Pa results only in a minor decrease of the energy input to 16.4 ± 0.3 eV. The functional dependence of the energy input on pressure is well described by linear fit curves. These are shown in Figs. 1(a) and 1(b). The extrapolation of the linear curves to zero pressure results in values in the range of 10.8–16.1 eV for Al (Table I). No clear effect of power on these extrapolated values can be observed. For Si the extrapolation results in an energy of 17.6 eV at zero pressure. The observation of a pressure-dependent energy per atom is in contradiction with the measurements performed by Thornton.[7] He reported on a pressure-independent energy flux in the range between 0.13 and 1.3 Pa. In contrast, over the range from 0.2 to 1.0 Pa the measured values in Fig. 1 increase by a factor of about 2. Figure 2(a) shows for the sputter deposition of germanium also a linear increase of the energy input per atom with pressure. The linear extrapolation of the fit curves results in values of 24.5 and 21.0 eV for discharge powers of 50 and 500 W, respectively (Table I). As in the case of Al, the effect of pressure on the energy input decreases with increasing power of the discharge. There is only a weak increase of the energy per atom from 22.2 to 25.4 eV when the pressure increases from 0.25 to 1 Pa. This behavior, in contrast with the above results for Al and Si, is in agreement with Thornton's measurements.[7] The energy input as a function of pressure measured for molybdenum is also roughly described by a linear fit curve as shown in Fig. 2(b). The experimental findings for tungsten deposition [Fig. 3(a)] are quite different from the results for the other elements. For the lowest power of 20 W, there is also a linear increase of the total energy per atom with pressure (with the exception of the highest pressure values investigated, where the energy approaches a constant value—see Table I). At increased discharge power, the energy per atom is no longer a function of

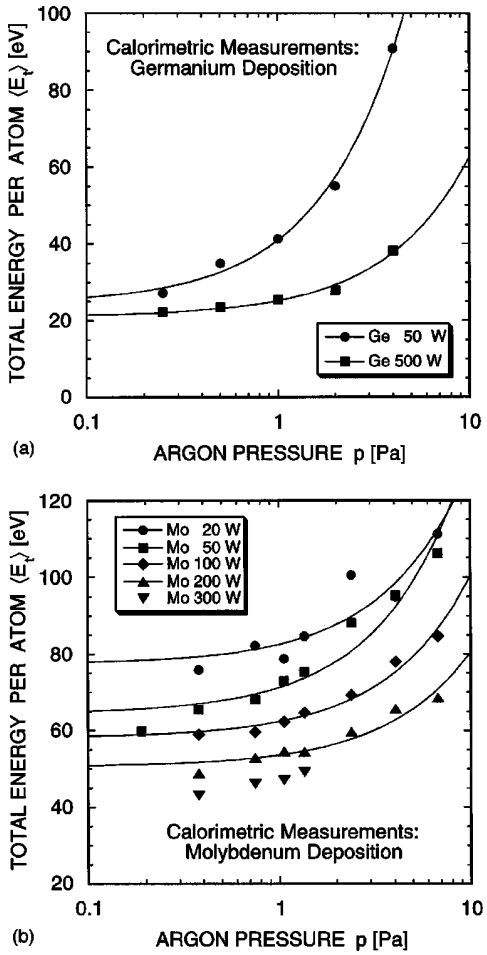

FIG. 2. Total energy input per atom as a function of argon pressure for (a) germanium and (b) molybdenum. The data were taken at different sputtering powers, which are given in the legend. The solid lines are linear fit curves.

pressure. In addition, the energy per atom is power independent and amounts to 136 eV. As a key experiment to rationalize the results of the calorimetric measurements, the experiment was repeated for molybdenum. However, the substrate was no longer kept at ground potential but biased with −30, −10 and +10 V versus ground. The result of the experiment is shown in Fig. 3(b). For negative potential, the measured values are always below the previously measured values. With the exception of the value taken at 7 Pa, the data points for −10 and −30 V are practically coincident. At the lowest pressure of 0.2 Pa, the data values coincide also with that taken at ground potential. By increasing the pressure from 0.2 to 1.0 Pa, the energy flux of the negatively biased sample does not increase in agreement with Thornton's results.[7] For the positive bias, the energy input shows a strong increase. From this experiment [Fig. 3(b)] it is clearly evident that, with the exception of the low-pressure region, the measured values of the energy per atom are affected by negatively charged particles.

IV. RESULTS: TRIM.SP SIMULATIONS

As a test for the results of the TRIM.SP calculations, the sputtering yields obtained are compared to experimental

yields from the early work of Laegreid and Wehner.[18] It is evident from Fig. 4(a) that for the selected elements (and also for the others, which are not shown) there is fair agreement between experiment and calculation. This test is considered as a hint for the reliability of the TRIM.SP simulations also for the other results discussed below.

A. Energy of sputtered atoms

The average kinetic energies of the sputtered atoms derived from the TRIM.SP simulation are shown in Fig. 4(b). As evident, the functional dependence of the average energy on the target voltage (projectile energy) is well described by a power law. Table II contains the parameters of the fit curves. With the exception of carbon, the powers are around 1/2 (in agreement with experimental observations[1]) and show a quadratic dependence on the target atomic mass with a minimum at 118 amu (see Table II). Because of the power-law dependence, there is only a small increase of the kinetic energies at voltages above 400 V. The average energies calculated agree well with the experimental values given by Thornton[7] and Dembovski *et al.*[19] This is an additional indication for the reliability of the calculations performed.

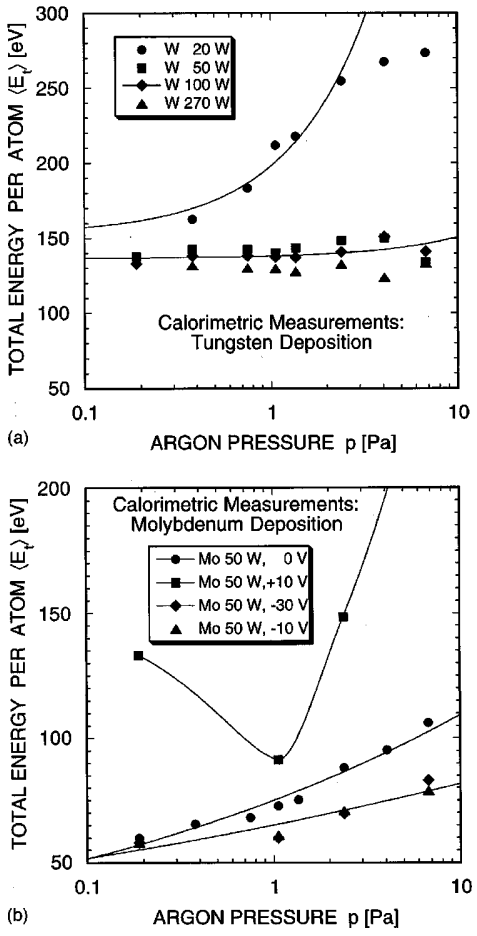

FIG. 3. Total energy input per atom as a function of argon pressure for (a) tungsten and (b) molybdenum. The data (a) were taken at different sputtering powers (see legend). The data (b) were taken at different substrate bias (see legend). The solid lines are fit curves.

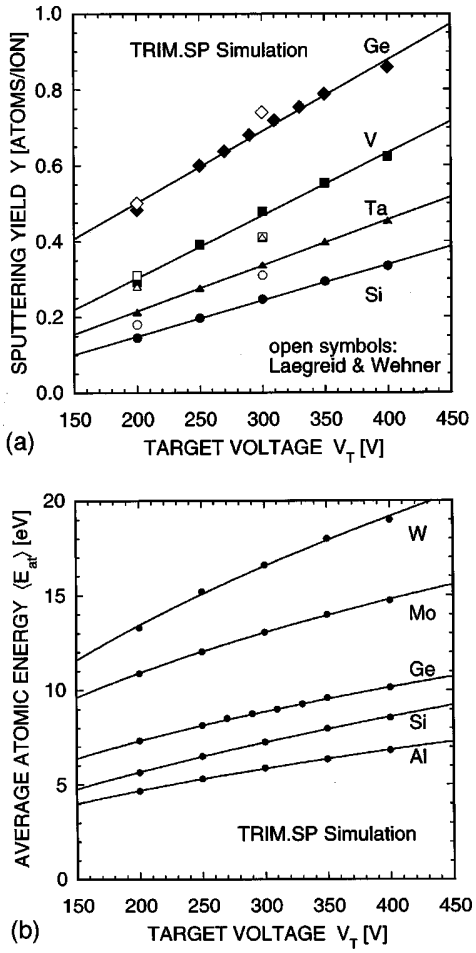

FIG. 4. Sputtering yields (TRIM.SP calculations) of selected elements as a function of target voltage in comparison to experimental data taken from the work of Laegreid and Wehner (a). The average energy of the sputter-ejected atoms of selected elements as a function of target voltage (b). The solid lines are linear (a) and power-law (b) fit curves, respectively.

In addition, the average energy of the sputtered atoms can be calculated in principle by an analytical integration for a given energy distribution $f(E)$ and the maximum transferred energy $E_{\max}$[16,20,21] by

$$\langle E_{\mathrm{at}}\rangle = \int_0^{E_{\max}} f(E)E\,dE \Big/ \int_0^{E_{\max}} f(E)dE,$$
$$f(E) = \frac{E}{(E+U_0)^{3+2m}}. \tag{3}$$

The potential parameter m for power interaction is chosen to be $m=1/6$.[22,23] U_0 is the surface binding energy.[15,24] Note that f is slightly different from the Thompson distribution,[1] which was derived under the assumption of hard sphere collisions $(m=0)$.

The energy distribution of the sputter-ejected atoms was found to satisfactorily obey the distribution function f. For projectile energies of 200 eV, the simulated energy distributions of the atoms start around energies equivalent to $3U_0$ to fall below the distribution function f. For projectile energies of 400 eV, the validity of the distribution function is ex-

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