Absolute sputtering yield of Ti/TiN by Ar^+/N^+ at 400–700 eV

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Ti and TiN films are used as diffusion barrier layers in Al and Cu metallization. They are often produced using physical-vapor-deposition techniques and are subject to energetic particle bombardment during subsequent processes. Therefore, the sputtering yield for ion-induced physical sputtering is important. The absolute sputtering yields of Ti and TiN target materials with 400–700 eV normally incident N and Ar ions are measured here. The experimental values are favorably compared to simulation results from TRIM.SP, which is a vectorized Monte Carlo code simulating ion–surface interaction using a binary collision mode. The phenomenon of reactive sputtering of Ti with incident N is also discussed. [DOI: 10.1116/1.1362678]

I. INTRODUCTION

Sputtering of target atoms from solid surfaces under ion bombardment has long been studied for both physical understanding of the collisional processes involved and for various physical reasons. Absolute sputtering yield data of metals and semiconductors are of practical interest in surface cleaning, etching, and sputter deposition devices. In the microelectronics industry, which utilizes various types of low-energy plasma processes in the fabrication of semiconductor devices,[1] the understanding of fundamental low-energy ion/surface interactions is quite important. In very-large-scale-integrated (VLSI) interconnections, thin-film diffusion barrier layers are routinely employed to prevent the direct contact and intermixing of two reactive materials, e.g., Al and Si.[2] With device feature size decreasing, Al is replaced by Cu as an interconnect material. Cu has low resistivity and high reliability against electromigration.[3,4] However, Cu is known to have high diffusivity in Si and SiO_2, and when it is dissolved into silicon at interstitial sites, it becomes a deep-level dopant[5,6] or forms neutral B–Cu complexes in the case of boron-doped silicon.[7,8] TiN/Ti is presently one of the most widely used barrier/contact materials in Cu metallization, as well as in aluminum-based metallization.[9–11] Typically, the barrier and adhesive layer is sputter deposited in an ionized physical-vapor-deposition (IPVD) magnetron system with Ti as target material.[12,13] This article deals with the measurements and modeling of the sputtering yield of Ti/TiN samples by Ar^+ and N^+ beams at normal incidence and low energies. This will help in understanding the physical and chemical processes inside an IPVD system. The use of N^+ as the incident ion beam is particularly interesting as it gives us insight into the reactive sputtering processes in the magnetron.

II. EXPERIMENT

The schematic diagram of the ion–surface interaction experiment (IIAX) facility, designed to measure the absolute sputtering yield, is shown in Fig. 1. An ion beam is generated in a Colutron plasma-based ion source.[14,15] The ion is accelerated by applying a potential drop of 700 V, focused by a three-element cylindrical electrostatic lens and charge-to-mass selected by an $E\times B$ filter. The single-species ion beam then enters the main chamber and is decelerated to the required energy by a five-element electrostatic beam and decreases its intensity. The beam is transported at energy of 700 eV, so that the velocity of the ions is fairly high as they transit the system from source to target, and the time of this interaction is minimized (10 ms). The neutrals are removed from the beam by an electrostatic neutral filter, which works by deflecting the ions in a parallel and unobstructed path. The beam hits the target at normal incidence. The target is fixed and the ion beam is fine focused by the electrostatic lens and decelerator combination. The sputtered atoms are collected on a quartz-crystal microbalance (QCM) deposition crystal. The QCM has two crystals, a deposition crystal and a reference crystal. It is mounted on the manipulator, and thus its spatial and angular position with respect to the target is known. The change in frequency of the deposition crystal with respect to the reference crystal gives a measure of the amount of mass loss due to physical sputtering of the target. A hollow-cathode source called a plasma cup is also mounted on the manipulator. It is used for the generation of Ar plasma for sample–surface clean up. This apparatus has been used in a number of other experiments.[16,17]

A high-purity Ti sample from Tosoh SMD, Grove City, OH, is used for the analysis. It is sputter cleaned by exposing the surface to the Ar plasma. The plasma removes the native-oxide layer and impurities by sputtering away several monolayers from the sample surface. A TiN sample is prepared by depositing TiN onto the silicon wafer in the IPVD magnetron system. The scanning electron microscope (SEM) micrograph shows the amorphous microstructure with 1.25 μm total deposition thickness. The observed morphology results in no preferred orientation of the deposited film, and thus its texture is quite poor and has no influence on the absolute sputtering yield.

The absolute sputtering yield is calculated by measuring the total ion dose and frequency change of the QCM depo-

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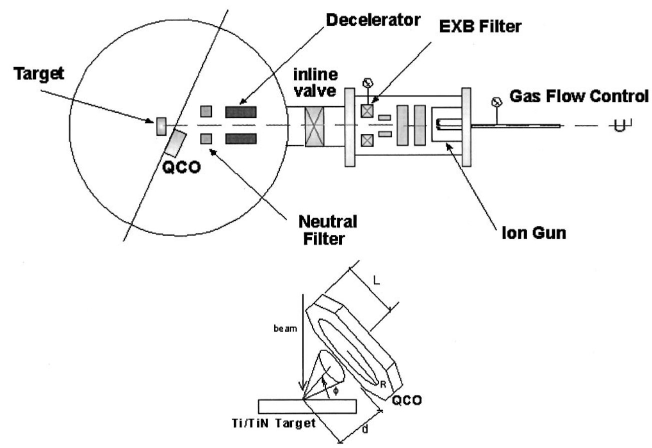

FIG. 1. Ion–surface interaction experiment (IIAX). The experimental device is shown with two differentially pumped chambers. On the right, the ion-gun chamber and on the left, the main chamber where the titanium or titanium-nitride target sample is located. Inset shows the quartz-crystal microbalance dual-control unit (QCM-DCU) with respect to the target holder.

sition crystal with respect to the reference crystal. The total ion dose is the total number of ions striking the target surface over time. The experiment is run for about 7–9 h at single-beam energy to improve the ion dose, which in turn decreases the error in the calculated yield value. The frequency of the deposition crystal decreases as the amount of sputtered material deposited increases. The frequency of the reference crystal is subtracted from the frequency of the deposition crystal to remove any background noise in the data. This includes any reactive components during material deposition. The base pressure in the system is kept between 10^{-6} and 10^{-5} Pa and rises to about 10^{-4} Pa during bombardment, the largest component being the partial pressure of the beam species.

If D is the total ion dose, Y the sputtering coefficient, Ω the fraction of the normalized cosine distribution of sputtered particles subtended by QCM, m_{target} the mass of target atoms, and S the sticking coefficient for the sputtered atom on the crystal, then the mass deposited on the crystal corresponding to the mass loss from the target due to physical sputtering is

$$M_d = DSY\Omega m_{\text{target}}. \tag{1}$$

If Δf is the change in frequency, f_{final} is the final frequency, and M_{crystal} is the mass of the crystal, then the mass deposited on the crystal calculated by measuring the change in frequency of the QCM is

$$M_{\text{QCM}} = \frac{\Delta f}{f_{\text{final}}} M_{\text{crystal}} (1 + R_j Y_j^{\text{QCM}} \Omega_j), \tag{2}$$

where R_j is reflection coefficient of incident atoms, Y_j^{QCM} is the sputtering coefficient of energetic neutrals impinging on the deposition crystal surface, Ω_j is the corresponding solid angle subtending these reflected neutrals, and j denotes the species type. The additional term in the bracket is due to resputtering of target atoms sticking to the QCM by reflected neutrals (from the incident ion beam) from the target surface. The reflected flux from the Ti and TiN samples has average energies between 20 and 70 eV for the incident energies of our concern. At these low energies, resputtering from QCM is extremely low and the additional term is neglected. Equating the two terms M_d and M_{QCM}, solving for the sputtering yield coefficient Y, we have

$$Y = \frac{1}{DS\Omega m_{\text{target}}} \frac{\Delta f}{f_{\text{final}}} M_{\text{crystal}}. \tag{3}$$

Equation (3) needs modification for the sputtering yield analysis of the TiN target. The two components, titanium and nitrogen, do not have the same partial sputtering yields. There is preferential sputtering of nitrogen from the TiN target. Also, the sticking coefficient of titanium is different from the sticking coefficient of nitrogen on the deposition crystal. Using separate yield (Y), sticking coefficient (S), and atomic mass (M) terms for titanium and nitrogen, M_d can be rewritten as

$$M_d = D\Omega (Y_{\text{Ti}} S_{\text{Ti}} M_{\text{Ti}} + Y_{\text{N}} S_{\text{N}} M_{\text{N}})/N_A, \tag{4}$$

with N_A, Avogadro's number, 6.02×10^{23} atom/mol.

Now, we also need to know the ratio of the partial yields of titanium and nitrogen to solve the above set of equations to calculate the absolute yield of titanium. We have used TRIM.SP (Ref. 18) simulation to find the ratio

$$\frac{Y_{\text{N}}}{Y_{\text{Ti}}} = r. \tag{5}$$

The ratio depends upon the target material composition, and energy and characteristics of the incident ion beam. If the target is nitrogen enriched, the ratio will be higher. If the target is nitrogen deficient, then the ratio will be lower. If we start from a titanium-nitride sample having atomic concentration of 50% Ti and 50% N, at the end, the target surface will still have more Ti than N because of preferential sputtering of N. TRIM.SP does not take into account the change in composition during the sputtering process. So, we need to be careful about choosing the target composition while running the simulation. This, in turn, will affect the value of r. The x-ray photoelectron spectroscopy analysis done after the experiment shows little or no nitrogen on the target surface. So, there is a continuous change in composition of the target surface during the sputtering and reformation process. It changes from 50% Ti–50% N to almost 100% Ti. Considering the factors above, we have chosen a composition of 75% Ti–25% N on the target surface, while estimating the ratio r. The large uncertainty in the target composition introduces a large uncertainty in r, which is taken into account in the error analysis. Doing a mass balance as before, the absolute sputtering yield of Ti is given by

$$Y_{\text{Ti}} = \frac{N_A}{D\Omega (S_{\text{Ti}} M_{\text{Ti}} + r S_{\text{N}} M_{\text{N}})} \frac{\Delta f}{f_{\text{final}}} M_{\text{crystal}}. \tag{6}$$

TRIM.SP (Ref. 18) is a Monte Carlo code, which simulates the ion–surface interaction using a binary collision mode and calculates the physical sputtering, reflection, energy deposition, and three-dimensional trajectory of energetic particles. It is an extension of the program TRIM (transport of ion in

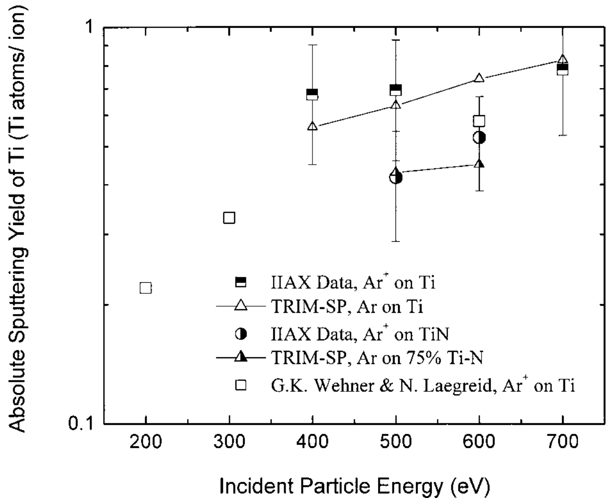

FIG. 2. Absolute sputtering yield of Ti data from Ar^+ bombardment on Ti and TiN targets in the range of 200–700 eV at normal incidence and TRIM.SP simulation.

matter)[19] and uses exclusively elastic kinematics. This program is vectorized, which means that instead of following one atom at a time, many particles can be treated in parallel. TRIM.SP also supports simulations for multicomponent targets. The simulations were completed for 10 000 histories at various energies. The heat of sublimation of Ti was used for the surface binding energy with a value of 4.89 eV. The heat of formation was used as the binding energy of the TiN target, with a value of 4.94 eV.[20]

III. RESULTS

Figure 2 shows the experimental and computational results for Ar^+ on titanium and titanium nitride at normal incidence. Figure 3 shows the results for N^+ on titanium and titanium nitride. All the values correspond to the absolute sputtering yield of titanium. Table I summarizes the data points with the corresponding experimental errors. In Table I, the data points for Ar^+/N^+ on TiN from TRIM.SP simulations correspond to the target composition of 75% titanium and 25% nitrogen.

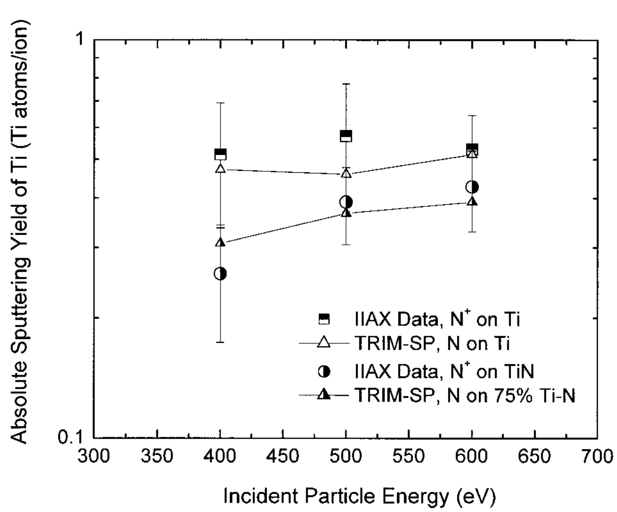

FIG. 3. Absolute sputtering yield of Ti data from N^+ bombardment on Ti and TiN targets in the range of 300–700 eV at normal incidence and TRIM.SP simulation.

Of all the cases, Ar^+ on Ti shows the highest absolute sputtering yield. Experiments with Ar^+ on Ti were straightforward. Simulation results match very well with experimental values for this case. The data points obtained by Laegreid and Wehner[21] are about 10%–20% lower from the TRIM.SP simulation. Considering the extrapolation in energy and experimental error in IIAX points, these data are relatively comparable. For the TiN samples, there is preferential sputtering of nitrogen. The surface composition profile changes continuously during the course of the experiment. At low energy, large numbers of interactions are very near the surface, thus modeling becomes very difficult for these cases. The surface becomes nitrogen deficient due to preferential sputtering of nitrogen. As Figs. 2 and 3 show, the simulation results are within the error range of experimental data points. For the N^+ incident beam, Ti combines chemically with N ions/atoms to form TiN, changing the target composition during the course of the experiment. But, it is known that this compound can form only when the incident nitrogen has a very low energy in the range of the thermal energy. At the energies in which our experiments are carried out, nitrogen has to go deep in the target before it loses its energy in the thermal energy range. So, there is no significant amount of TiN formed at the target surface even though the absolute sputtering yield of Ti for this experiment could be expected to be slightly higher than the observed values.

IV. DISCUSSION

The absolute sputtering yield is weakly dependent on the incident ion-beam energy in this low-energy range. Ar^+ on Ti has the highest sputtering yield values of Ti at all energies. It is, on average, 1.2 times higher than N^+ on Ti. This is due to the fact that the atomic weights of Ti and Ar are comparable, resulting in a higher-energy transfer from the incident ion to the target atom. Reactive sputtering for the incident nitrogen beam is another reason, even though it is not a major factor here. The sputtering yield of Ti from the TiN target is about 1.5 times lower than the pure titanium target for both argon and nitrogen beams. The difference in yield of Ti is more pronounced at lower energies because the ratio becomes larger with a decrease in the incident ion-beam energy. The combined yield of titanium and nitrogen from the TiN target is higher than the yield of titanium from the pure titanium target.

The lower sputtering yield of Ti from the TiN surface implies that the sputtering rate and, hence, the deposition rate of the films grown in poison mode in an IPVD system will have a lower value compared to films grown in metallic mode, where the target surface remains pure Ti. The partial pressure of nitrogen in the IPVD system will have a significant influence on the deposition rate of the films because nitrogen has a twofold effect: it will alter the surface composition profile of the target making it more nitrogen rich

TABLE I. Experimental and TRIM-SP simulation results for the absolute sputtering yield of Ti from Ar and N bombardment of Ti and TiN targets.

	Energy (eV)	IIAX (atoms/ion)	TRIM.SP (±3%)
Ar^+ on Ti	400	0.676±0.227	0.560
	500	0.694±0.234	0.634
	600		0.741
	700	0.782±0.248	0.827
Ar^+ on TiN	500	0.417±0.129	0.429
	600	0.527±0.142	0.450
N^+ on Ti	400	0.514±0.178	0.471
	500	0.571±0.202	0.459
	600	0.530±0.114	0.514
N^+ on TiN	400	0.258±0.084	0.307
	500	0.391±0.086	0.366
	600	0.427±0.098	0.391

and, it will dilute the amount of argon, the species which is not efficient at sputtering. The N^+ beam used in the IIAX experiments does not cause any significant amount of TiN formation on the Ti target surface. This implies they must be neutral N atoms, which have energies in the thermal range, leading to TiN formation in the IPVD system and not energetic N^+ ions. Therefore, from both of these observations, the metallic-mode sputtering should, and does, produce higher deposition rates, yet both the poison and metallic modes can make stoichiometric TiN.

V. CONCLUSION

The absolute sputtering yield of Ti for Ar^+ and N^+ bombardment of titanium and titanium-nitride targets has been measured at relatively low energies in the range of 200–700 eV. The sputtering yield of Ti is found to be lower for the TiN target when compared to the Ti target. Preferential sputtering of N from TiN leads to this result. The lower yield of titanium from the TiN target conclusively establishes the fact that it is advantageous to operate an IPVD system in the metallic mode, rather than the poison mode.

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