Gasless sputtering: Opportunities for ultraclean metallization, coatings in space, and propulsion

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Abstract

Pulsed magnetron sputtering was demonstrated in high vacuum: no sputter gas was used at any time. Sustained selfsputtering was initiated by multiply charged ions from a short vacuum arc. Copper ion currents to an ion collector in excess of 30 A were measured, implying a plasma density of about 6×10^{18} m^{-3}. This technology may prove useful for metal coatings free of noble gas inclusions and suggests that magnetrons could operate in the vacuum of space. In addition to coating objects in space, the momentum of the sputtered atoms and ions may be utilized in space thrusters.

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Magnetron sputtering using gas plasma is a common method for thin film deposition with a wide range of applications including semiconductor manufacturing, large area glass coatings, automotive and tool coatings. The gas ions serve two purposes: sputtering, i.e. the removal of surface atoms from the sputter target, and the generation of secondary electrons which, when accelerated by the sheath voltage, sustain the electron temperature and ionization processes. Generally, the sputtered atoms remain neutral unless special conditions lead to a high probability of ionization. At relatively high pressure the gas can be used to slow down the sputtered metal atoms by collisions, thereby increasing their chance of ionization (also known as i-PVD[1]).

Unfortunately, the sputter gas can also cause problems. For example, its inclusion in the growing films can alter film structure and cause a reduction of the electrical conductivity.[2,3] One important development has therefore been sustained selfsputtering. Selfsputtering is sputtering caused by an ion of the same element constituting the sputter target. In *sustained* selfsputtering, the process can operate by selfsputtering only, i.e., after the noble gas needed to start the discharge has been pumped out. This was demonstrated using a magnetron in cylindrical[4] and planar[5] geometry. Sustained selfsputtering can only be accomplished at high power densities, and therefore needs exceptionally well-cooled magnetrons.

It is known that ion assisted deposition facilitates control of film structure, density and adhesion and therefore, in many applications, it is desirable to have a high ion-to-neutral ratio. The direction and energy of ions arriving at the surface can be affected by the application of bias, which is imperative for trench and via filling in microelectronics.[1]

The straight-forward way of increasing ionization is to increase power density. This approach is primarily limited by cooling constraints. The recent development of high power impulse magnetron sputtering (HIPIMS) circumvents the constraint by pulsing with a relatively low duty cycle[6,7] so that the average power can be kept within the typical design limit of a magnetron. In this way, very high instantaneous power pulses are possible and high levels of metal ionization have been achieved.[6,8-10]

Despite having a large component of selfsputtering, conventional HIPIMS cannot be operated without gas due to its pulsed nature. If the gas was removed from the system, selfsputtering could only be maintained at very high power levels, posing a tremendous challenge on cooling. With the low duty cycles typically used to allow high power pulses, the plasma would decay after a pulse beyond recoverability and the next pulse would not ignite. In this contribution, we will demonstrate a solution to this issue.

Singly charged metal ions cannot generate a sufficient amount of secondary electrons; the presence of multiply charged metal ions was shown to be a necessity for maintaining metal selfsputtering.[11-13] Hence, if multiply charged ions were supplied to a magnetron target with a voltage above the selfsputtering runaway threshold[11,12], the sputter yield as well as electron emission yield should be sufficient to initiate and sustain selfsputtering, even in the absence of any sputter gas. Thereby gasless, high power pulsed magnetron sputtering would be possible, enabling ultra-clean metal coatings, sputtering in space (previously thought impossible) and perhaps even space propulsion that uses a non-combustible solid “fuel”.

This type of process was demonstrated for copper using the setup shown in Figure 1. A short (~20 µs), ~200 A, vacuum-arc discharge[14] was used to supply plasma with multiply charged ions to initiate the magnetron selfsputtering discharge. The magnetron voltage was applied simultaneously with the arc discharge. The magnetron discharges were initiated at a very low pulse repetition rate of 1-5 pulses per second, allowing sustained selfsputtering to operate with comparably long pulses of several milliseconds.

An example of arc and magnetron discharge current is shown in Fig. 2. After the arc discharge is over, the magnetron discharge not only self-sustains, but in fact self-*amplifies* via selfsputtering runaway[4,11-13] towards a steady state at a higher discharge current.

In complimentary measurements using the sputter target as a probe (biased to -50 V) for the pulsed arc plasma, the peak ion saturation current from the arc discharge was less than 4 A. The experiment also showed that there was no ion current from the arc discharge 10 μs after its termination.

The effect of varying the magnetron pulse voltage is illustrated in Fig. 3a. Lower voltage means lower peak magnetron discharge current and a shorter pulse. The reduced pulse length is due to the diminished charge stored in the pulsing unit capacitors at lower voltages. At less than 550 V, the discharge is typically not able to sustain itself. The offset from the zero-line after the pulse is an artifact of the inductive current pick-up coils. For all of the selfsputtering pulses, the discharge ends at a voltage of 507 V (±2 V, 3σ), corresponding to a minimum power density of 540 W/cm^2.

The ion current to the negatively biased collector is presented in Fig. 3b. The general behavior follows that of the magnetron discharge, albeit at lower currents. Remarkably, the peak sample current, about 33 A, is 43% of the corresponding peak magnetron discharge current (77 A). Assuming space-charge limited current, a plasma electron temperature of 2.5 eV (leading to a Bohm velocity of about 2000 m/s) and an average ion charge state of 1.5, this ion current corresponds to a plasma density of approximately $6\times10^{18}\ \mathrm{m}^{-3}$. The sample ion current from the arc discharge alone was about 0.3A, i.e. an insignificant contribution compared to the magnetron discharge.

The background pressure of the chamber was about 10^{-4} Pa (high vacuum), and no gas was added to facilitate the discharge. There is no reason the demonstrated process could not run in better vacuum, even in the extreme high vacuum of space. To clarify: during the magnetron pulse, of course there is the pressure of metal vapor, hence the sputter process itself is not running in vacuum but in a pure copper vapor and plasma. The fraction of neutrals in the plasma is interesting and may be of importance to some applications, but is unfortunately difficult to measure. This fraction can be relatively high for materials of high sputter yield, like the copper used here.

The system in this demonstration was triggered at low pulse repetition rates. Scaling to higher repetition rates is straight-forward. HIPIMS processes are routinely run at hundreds of pulses per second and similar arc pulse repetition rates have also been demonstrated.[15] The limitation is the cooling of the average magnetron power which is set by current, voltage and duty cycle.

At high power, when the metal ion current is large and no background gas is present, the process is similar to a vacuum arc from a deposition point of view. However, there are two distinct advantages: much less macroparticle contamination and the possibility of scaling to larger areas. The small risk of macroparticle contamination from the short trigger pulse can be further reduced by using a filter on the arc source. Particles from the magnetron are reduced by utilizing the arc-suppression built into the power supply, i.e., when an arc event is detected the power supply rapidly turns the voltage off. The deposition area is readily enlarged by increasing the target area and scaling the power supply accordingly.

The underlying assumption that led to the realization of this process is the necessity and possible sufficiency (above a threshold voltage) of multiply charged ions for sustained self-sputtering. These could also be produced by a high power laser pulse. Hence, it is believed that also laser ablation of a metal in the vicinity of the magnetron target can be used to initiate the HIPIMS discharge.

The most obvious use of the process is to make ultraclean, high density metal coatings through self-ion-assisted deposition. The high degree of ionization renders the application of substrate bias highly efficient, suggesting that it can be used for trench and via filling in semiconductor manufacturing. Another potential use is metallization in space, for example production of solar reflectors, and recoating of reflective surfaces or solar shades, as was previously suggested for pulsed cathodic arcs.[16] The momentum on the magnetron from the sputtered atoms could be used to produce thrust for space propulsion. Since sputtered atoms and ions have a higher velocity than arc macroparticles of the same material, the solid fuel (i.e. target) might be better utilized by vacuum HIPIMS than the fuel of an arc thruster (cathode). In contrast to conventional xenon arc thrusters, the HIPIMS "fuel" can safely be stored without heavy and costly tanks.

In conclusion, a high power impulse magnetron sputtering process in high vacuum has been demonstrated for copper. The need for process gas was eliminated by providing a short (20 μs) puff of metal plasma to the target; the triggering plasma was produced by a pulsed vacuum arc containing multiply charged ions. The magnetron, operating in the pure selfsputtering mode for milliseconds, provided a large flux of metal ions to an ion collector. Measurements of the ion saturation current indicated a very high plasma density at the ion collector position of about $6\times10^{18}\ \mathrm{m}^{-3}$. Such metal plasma may be utilized for the deposition of ultrapure, dense metal films as well as for space propulsion using a solid, non-combustible and non-toxic fuel.

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Figure 1. (Color online) A miniaturized arc plasma source (“minigun” Ref. 14) with a copper cathode was aimed at a 2”, nominally balanced magnetron loaded with a copper target. The magnetron power was supplied by a high current pulsed DC-generator (SPIK 2000A, Melec), charged by an Advanced Energy Pinnacle DC-supply. A metal block (110 cm^2 area facing the magnetron) used as an ion collector was placed 10 cm from the target and biased to -50 V. The initiating arc discharge, magnetron discharge, and sample currents were measured with high bandwidth coils and recorded by a digital oscilloscope. The magnetron discharge voltage was also recorded via a 100:1 fast voltage divider. The chamber was pumped by a cryopump and the experiments were made at the chamber background pressure of 1.1×10^{-4} Pa , i. e. in high vacuum.

Figure 2. (Color online) The initial, ~20 μs, high-current pulse is the arc discharge current that triggers the long duration, ~3-9 ms, magnetron discharge. The inset emphasizes the triggering event of the magnetron discharge. The total charge moved by the arc discharge is about 1% of that moved by the magnetron discharge. Initially the magnetron voltage is 750 V. The maximum power density of the magnetron discharge is in excess of 3 $kWcm^{-2}$. The current decrease is due to discharging of the storage capacitors of the pulsing unit.

Figure 3. (Color online) Time dependence of (a) the magnetron discharge current and (b) ion collector current for a series of different initial discharge voltages. The discharge does not initiate sustained selfsputtering when the target voltage is less than 550 V.

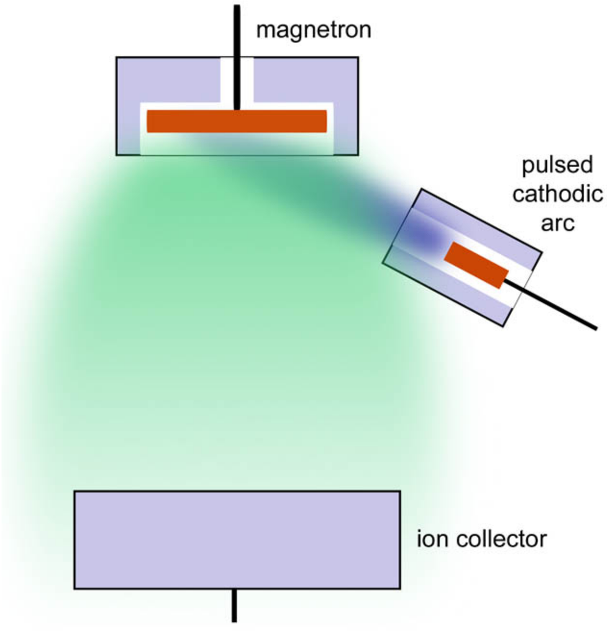

Fig. 1

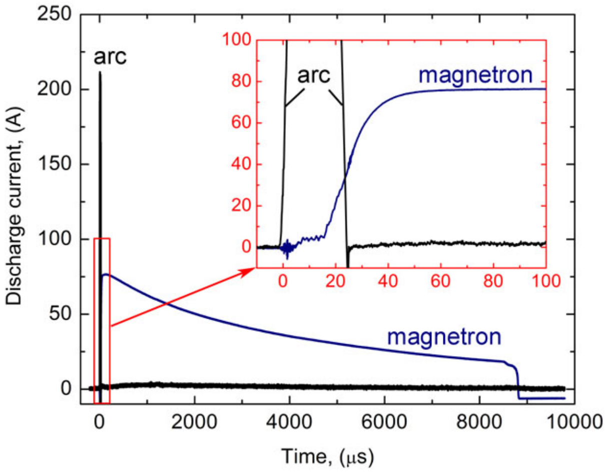
250
200
150
100
50
0
arc
magnetron
Discharge current, (A)
0
2000
4000
6000
8000
10000
Time, (μs)
100
80
60
40
20
0
0
20
40
60
80
100
arc
magnetron

Fig. 2

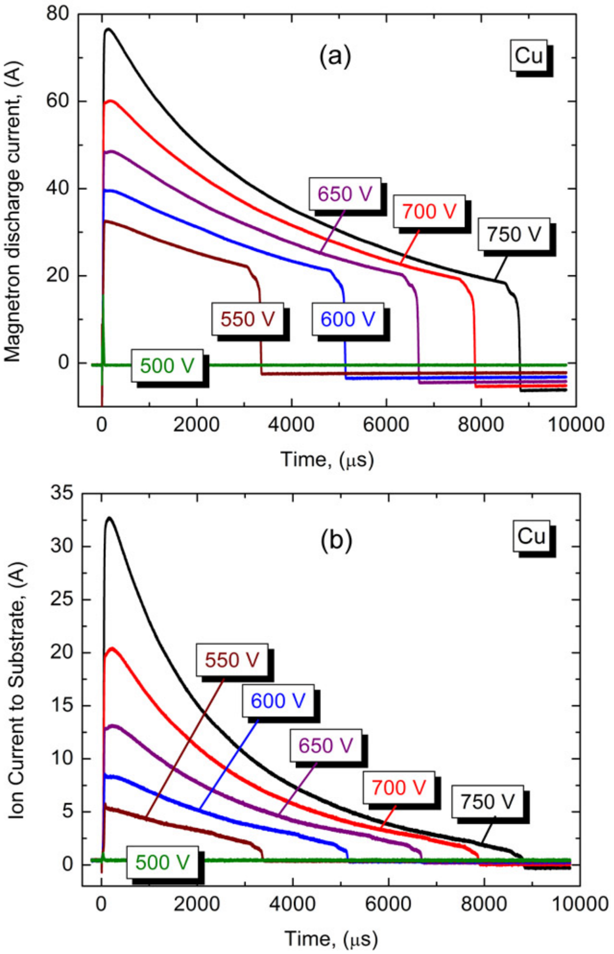
(a)
Cu
Magnetron discharge current, (A)
80
60
40
20
0
0
2000
4000
6000
8000
10000
Time, (μs)
650 V
700 V
750 V
550 V
600 V
500 V
(b)
Cu
Ion Current to Substrate, (A)
35
30
25
20
15
10
5
0
0
2000
4000
6000
8000
10000
Time, (μs)
550 V
600 V
650 V
700 V
750 V
500 V

Fig. 3