Pergamon

Vacuum/volume 51/number 4/pages 641 to 646/1998

0042 207X/98 $ see front matter

PII: S0042-207X(98)00265-6

High-rate reactive DC magnetron sputtering of oxide and nitride superlattice coatings

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Over the past 10 years, there have been three major advancements in reactive sputtering technology that now make it possible to deposit both conductive and non-conductive fully-dense films at high rates. These three advances are unbalanced magnetron sputtering, partial pressure control of the reactive gas, and pulsed dc power. Multicathode unbalanced magnetron sputtering systems provide a dense secondary plasma that is used for producing a well-adhered, fully dense film that is difficult to achieve with conventional magnetron sputtering. Online automatic partial pressure control of the reactive gas prevents the poisoning of the target surface during deposition, which leads to compound film deposition rates that approach or are equal to those for the pure metal rate. Pulsed dc power, where the polarity of the voltage on the sputtering target is alternately switched briefly between negative and positive, prevents arcing on the target surface during the deposition of nonconducting films. With both pulsed dc power and partial pressure control of the reactive gas, films such as aluminum oxide can now be deposited reactively at rates up to 78% of the pure metal rate. The reactive unbalanced magnetron sputtering process is used to deposit polycrystalline nitride superlattice films such as TiN/NbN or TiN/VN with hardnesses exceeding 50 GPa, which is more than double the hardness of either component in the multilayered film. The nitride superlattice work is being extended to oxide films, and initial results are encouraging. Nanometer scale, multilayer Al_2O_3/ZrO_2 and Y_2O_3/ZrO_2 films have been deposited at high rates. The Al_2O_3/ZrO_2 films are amorphous and optically clear, whereas the Y_2O_3/ZrO_2 films are crystalline as well as being optically clear. © 1998 Published by Elsevier Science Ltd. All rights reserved

Introduction

Since the middle 1980s, there have been three major advance ments in sputtering technology that have greatly affected the ability to reactively sputter fully dense, well adhered films at high deposition rates. In 1986, Window and Savvides[1–3] intro duced the concept of unbalanced magnetron sputtering, and in the years since, it has been widely embraced by the sputtering community. Combined with partial pressure control of the reactive gas during the reactive sputter deposition of coatings, unbalanced magnetron sputtering today is one of the primary techniques for the deposition of hard coatings.

Most recently, the introduction of pulsed direct current (dc) power is already having an important effect on the reactive sputtering of non conducting films such as aluminum oxide (Al_2O_3). The combination of partial pressure control of the reactive gas, unbalanced magnetron sputtering, and pulsed dc power is a powerful tool for the high rate reactive deposition of compound films. Each of these three techniques will be reviewed, and then they will be looked at together to show the full potential for the synergistic effects for the deposition of non conducting films.

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Unbalanced magnetron sputtering

A conventional magnetron sputtering cathode has magnets located along the outer edge and the centerline or at the center if the cathode is round. If the strength of the inner and outer magnets is roughly equal, the magnetron is said to be balanced, and most of the magnetic field lines will loop between the inner and outer magnets as is shown in Figure 1. If one of the sets of magnets is made stronger than the other, then the magnetron becomes unbalanced. Typically the outer set of magnets in the magnetron cathode is made stronger than the inner ones. Although there is still linkage between magnetic fields of the inner and outer magnets, not all of the field line will make the link. The excess field lines from the stronger magnets will radiate away from the magnet surfaces as is shown in Figure 2.

During magnetron sputtering, energetic electrons escape from the primary magnetic trap between the inner and outer magnets, and in a balanced magnetron, these electrons go to the anode. It is the primary electron trap that is responsible for the formation of the dense plasma directly in front of the sputtering target and for the high deposition rate of the mag netron cathode compared to a diode cathode.

In an unbalanced magnetron, the escaping energetic elec trons are trapped by the excess magnetic field lines, and the

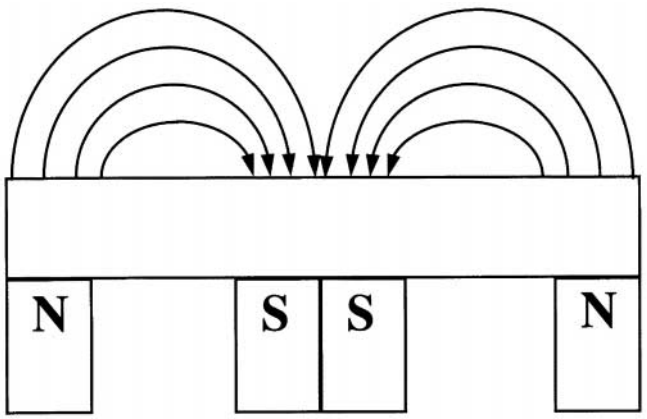

Figure 1. Schematic drawing of a balanced magnetron sputtering cath ode.

electrons spiral along the field lines and undergo ionizing col lisions with gas atoms. A secondary plasma is formed away from the target surface from these ionizing collisions, and this secondary plasma can be used for ion assisted deposition of the growing film. The current density collected on the sub strate during unbalanced magnetron sputtering is usually an order of magnitude higher than it is in conventional balanced magnetron sputtering, and substrate current densities are typi cally 5 10 mA cm^{-2} with unbalanced magnetron sputtering. These current densities match or exceed the substrate current densities found in other ion assisted deposition techniques.

When multiple unbalanced magnetron cathodes are used in the same chamber, it is important to link their magnetic fields in order to maximize the trapping of electrons. In an opposed, two cathode system, the polarity of the outer and inner mag nets on one cathode should be opposite to that polarity of the magnets in the cathode that it is facing; i.e., north pole should face south pole and vice versa. The magnetic trap cannot be complete if an odd number of cathodes are used. It is necess

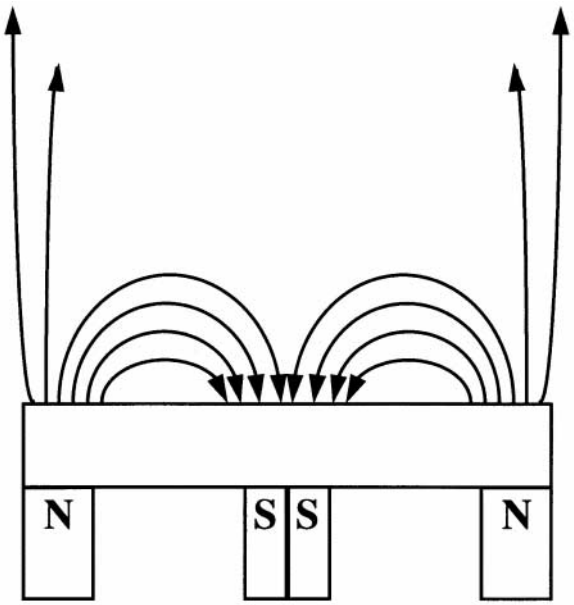

Figure 2. Schematic drawing of an unbalanced magnetron sputtering cathode.

ary to have an even number of cathodes to prevent a hole in the magnetic trap.

Four cathode rectangular unbalanced magnetron systems link magnetic fields with the cathode next to it and not to the one opposite it in the chamber. This linking provides good magnetic trapping of the electrons in one plane, but not in another. At the top and bottom of the cathodes, the magnetic field lines are in opposite directions, and there are holes in the magnetic trap. To overcome this problem, steel plates are placed at the top and bottom of the cathodes, and an electro static charge on these plates prevents the electrons from escap ing from the trap. The electrostatic charge can come simply by letting the plates electrically float in the plasma.

Ion assisted deposition is very important for forming fully dense, well adhered hard coatings. Both the ion current den sity and the ion energy (bias voltage) play significant roles in ion assisted deposition. In balanced magnetron sputtering, the ion current density is limited, and what is lacking in ion cur rent density has to be made up with the energy of the arriving ions. Typical ion current densities in balanced magnetron sput tering are less than 1 mA cm^{-2}, which produces low ion to arriving neutral species ratios. High bias voltages can be used to overcome partially the low ion to neutral ratio, but high bias voltages produce more damage than can be annealed out by the ion energy input.

Unbalanced magnetron sputtering, by producing a dense secondary plasma around the substrate, provides a high ion current density, on the order of 1 5 mA cm^{-2}, and the ion energy does not have to be as high as it is in balanced magne tron sputtering. Ion to neutral ratios greater than one are often reported for the unbalanced magnetron sputtering of hard coatings such as titanium nitride. Fully dense coatings are usually produced when the negative substrate bias voltage is in the 100 150 V range.

Reactive sputtering

Reactive sputtering is the sputtering of a metallic target in the presence of a gas that will react with the metal atom ejected from the target surface. Historically mass flow control has been used to control the amount of reactive gas flowing into the chamber, but flow control of the reactive gas can lead to problems. If the target is set at a fixed power and the flow of the reactive gas is increased, initially all of the reactive gas will be consumed by the reaction with the metal.

However, a point is reached as is shown in Figure 3 (point A) for the reactive sputtering of titanium in an argon/oxygen atmosphere where the amount of reactive gas in the chamber is sufficient to react with the surface of the target. When this happens and the oxide compound covers the surface of the target (the target is said to be poisoned), the sputtering rate drops rapidly because the sputtering rate of the compound is much less than that for the metal. Since the rate has decreased, not as much reactive gas is consumed, and its partial pressure jumps rapidly from point A to point B as is shown in Figure 3. With flow control, it is very difficult to operate between points A and B, and there is a range of compositions that is forbid den between these two points.

Partial pressure control of the reactive gas overcomes the problems of the flow control.[4–6] Using a sensor such as a quadrupole mass spectrometer that can provide a quick feed

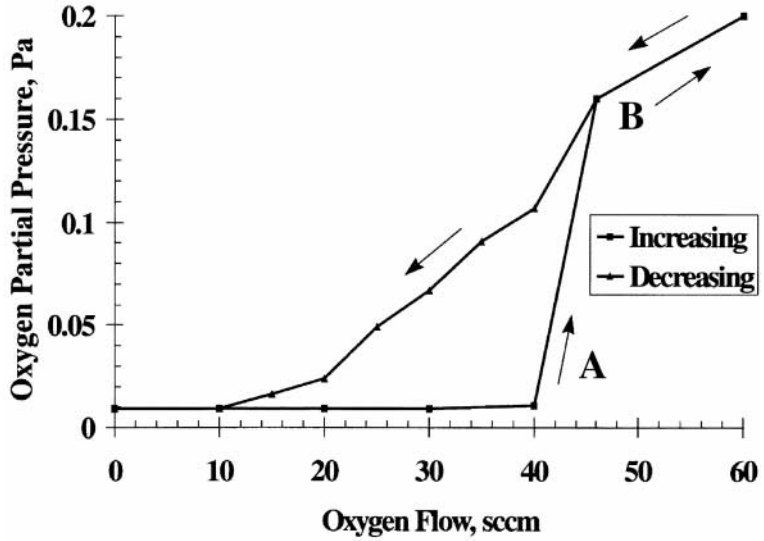

Figure 3. Hysteresis plot for the reactive sputtering of titanium in an argon/oxygen atmosphere with flow control of the reactive gas. The target power was 8 kW, and the total pressure during deposition was 1.1 Pa.

back signal for the partial pressure of the reactive gas, it is possible to control the partial pressure of the reactive gas at any desired set point as is shown in Figure 4 for the reactive sputtering of titanium in an argon/oxygen atmosphere. There are no forbidden compositions with partial pressure control, and it is possible to operate at any point between A and B in Figure 4. At point B, the target is fully poisoned, and the sput tering rate is very low. As the partial pressure is lowered toward point A, the deposition rate increases, and the chal lenge is to operate at as low a partial pressure that will pro duce the desired composition.

There are two main benefits of partial pressure control of the reactive gas. The first is that it is possible to reactively sputter hard compounds such as TiN at the same deposition rate as is found for the pure metal.[4] No higher rate can be achieved. Secondly, partial pressure control provides precise control of the composition of the compound, and it is possible to produce the same compound material in every run.

Reactive sputtering of oxides until just recently had been a difficult task. Oxygen reacts much more quickly with the target surface than does nitrogen, and it often forms an insulating compound on the target surface, which leads to difficulty in sputtering the desired material. When an insulating material forms on the surface of the sputtering target during depo sition, those insulating surfaces build up a charge and then dis charge during dc reactive sputtering, which results in arcing. This arcing is particularly violent for reactive dc sputtering of Al_2O_3, and it can result in damage to the power supply and liquid droplet ejection from the target surface.

Radio frequency (rf) power can be used for the reactive sputtering of oxides, but it has its own set of problems. Essentially half of the power is not used for sputtering, and

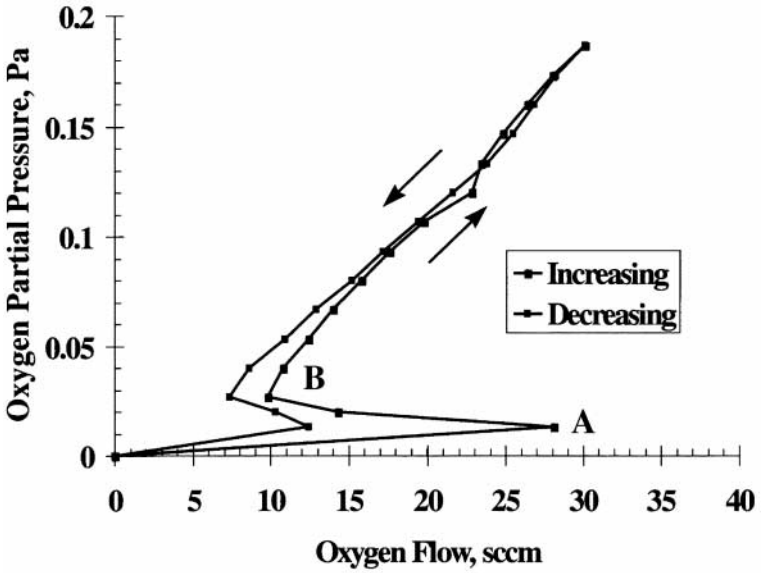

Figure 4. Hysteresis plot for the reactive sputtering of titanium in an argon/oxygen atmosphere with partial pressure control of the reactive gas. The target power was 5 kW, and the total pressure during deposition was 1.1 Pa.

the deposition rates for reactive rf power are much lower than that for the pure metal. For example, aluminum oxide reactive sputters with rf power at only 2 3% of the metal deposition rate.

One method used to overcome the problems of using dc power for reactive sputtering of nonconducting coatings is to shield the sputtering target from the reactive gas. Typically, the target is enclosed in a box, with a mesh screen over the target to let the sputtered atoms out. The argon sputtering gas is injected into the system next to the target, and the reactive gas is injected next to the substrate. Although this method does allow dc power to be used for the sputtering of noncon ducting coatings, the screen does reduce the sputtering rate since it intercepts part of the sputtered flux. Keeping the screen open is a problem with this method, and constant main tenance of the screen is required.

Pulsed dc power

Within the past few years, it has been shown[7–11] that bipolar pulsed dc power can be used for the reactive sputter deposition of oxides. With bipolar pulsed power, the polarity of the target power is switched from negative to positive, and during the positive pulse any charging of the oxide layer is discharged when electrons are attracted to the positive surface. During the negative pulse, ions are attracted to the target surface, and sputtering takes place initially from all surfaces on the target even those that have formed a compound since the charge on that surface has been neutralized during the positive pulse.

Bipolar pulsed power is classified as either symmetric or asymmetric, which refers to the pulse height in the positive and negative directions.[12] Symmetric bipolar pulsed dc power has equal pulse heights in both the positive and negative direc tions, as is shown in Figure 5, and the width of both the posi tive and negative pulses can be varied independently as can the time off between pulses. Symmetric bipolar pulsed dc power is often used for the reactive deposition of an oxide coating from two magnetron cathodes. These two cathodes, which are located side by side, are both connected to the same symmetric bipolar pulsed dc power supplied. One power lead goes to one cathode, and the other power lead is connected to the second cathode. With this electrical hookup, one sputtering target is the anode for the system, while the other is the cath

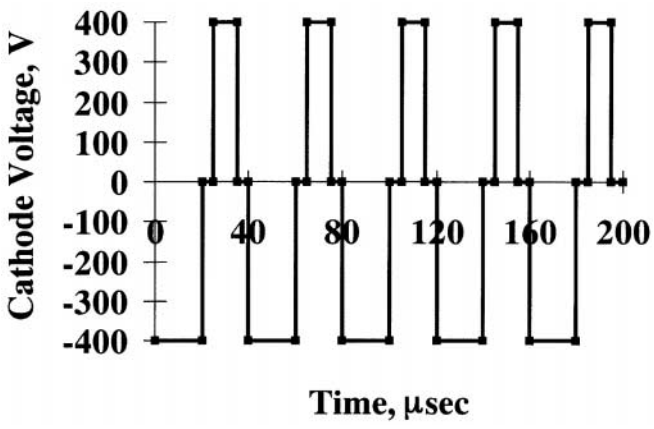

Figure 5. Schematic representation of symmetric bipolar pulsed dc power.

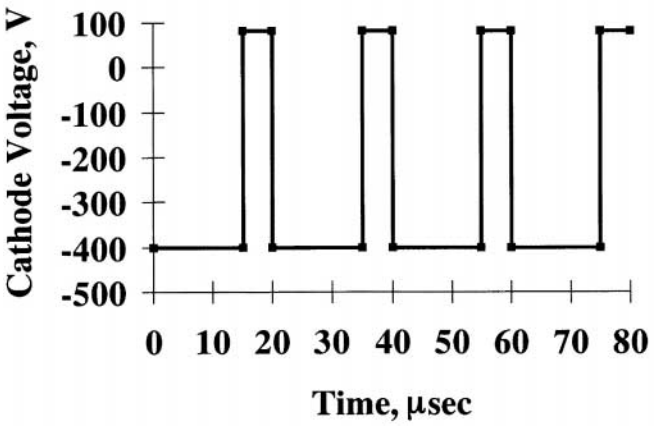

Figure 6. Schematic representation of asymmetric bipolar pulsed dc power.

ode. When the polarity of the voltage on the targets changes, the anode and cathode switch as well. Sputtering from the cathode surface during the negative pulse keeps the target sur face clean, and when it switches to act as an anode, it is not covered by an oxide. This procedure avoids the disappearing anode problem, which can occur in pulsed dc sputtering of ox ides when all surfaces in the chamber become covered with an insulating oxide.

Asymmetric bipolar pulsed dc power, on the other hand, has unequal pulse heights. The negative pulse height is greater than the positive one, and there is no off time between pulses as is shown in Figure 6. The width of the positive pulse is a fraction of the negative pulse width, and its width is usually 10 20% of the width of the negative one. A significant portion of the power cycle is spent in the sputtering mode, and the de position rate from asymmetric power can be close to that of pure dc power. The frequency of pulsed dc power covers a wide range from 0 (normal dc) up to 250 kHz, and typical operating frequencies for the pulsed dc power during reactive sputtering of oxides are in the 20 100 kHz range.

The frequency selected is a function of the material being reactively sputtered. Whereas no arcing can be achieved for the reactive sputtering of titanium dioxide at a pulsing fre quency of 30 kHz, it takes a frequency between 50 and 70 kHz for all arcing to disappear for aluminum oxide.[11] With both partial pressure control of the reactive gas and asymmetric pulsed dc power, we have been able to reactively sputter aluminum oxide with no arcing at a frequency of 70 kHz.

Although in theory pulsed dc power has a rectangular wave form, in fact it does not. There can be overshoot in the nega tive pulse and ringing on the positive pulse as is shown in Figure 7. This overshoot can be significant, and the target vol tage shown on the power supply can be quite misleading.[13, 14] For the example shown in Figure 7, the average target voltage is about 450 volts, which was displayed on the front panel of the power supply, but in fact the peak to peak voltage was about 1500 volts. Such high voltages will produce much more energetic particles during part of the pulse cycle, and the effect of these energetic particles on the structure and properties of the coating is still being evaluated. Initially there has been no noticeable effect of these high energetic neutrals on the proper ties of the coatings, but there may be applications where this high energy could be detrimental. In many ways, the voltages

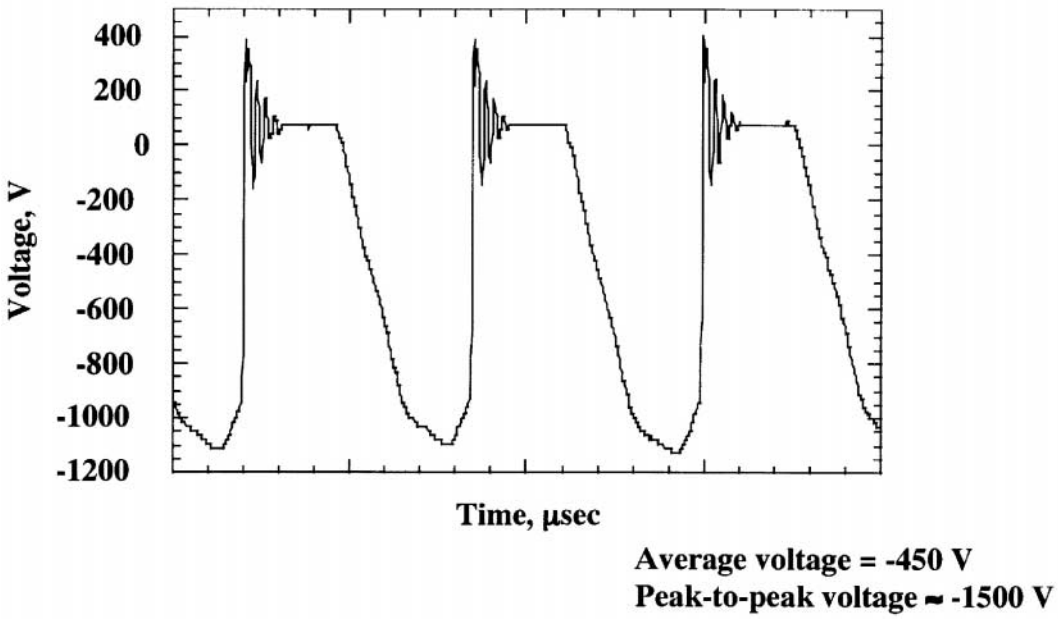

Figure 7. Trace of pulsed dc power during the reactive sputter of aluminum in an argon/oxygen atmosphere.

produced during asymmetric pulsed dc sputtering are similar to the voltages found in dc diode systems.

Reactive unbalanced magnetron sputtering of multilayered coatings

Reactive unbalanced magnetron sputtering in an opposed cathode system has been used very successfully to deposit nanometer scale multilayer nitride and oxide films that have enhanced physical properties.[15–19] The first work in this area was with titanium nitride/niobium nitride (TiN/NbN) and titanium nitride/vanadium nitride (TiN/VN) coatings. Partial pressure control of the reactive gas was crucial to achieve the cubic form of NbN, and the high degree of ion bombardment from the unbalanced magnetron sources led to fully dense well adhered films. The hardness of the TiN/NbN and TiN/VN films was greater than 50 GPa, which is more than twice the hardness of either component in these two multilayered films, when the superlattice period, which is the bilayer thickness of the TiN and NbN or TiN and VN, was in the range of 50 to 80 Å. The individual layer thicknesses were approximately equal.

The importance of the combination of pulsed dc power and partial pressure control of the reactive gas really came into the spotlight with the reactive unbalanced magnetron sputtering of non conducting oxides such as aluminum oxide (Al_2O_3). Without this combination of pulsed dc power and partial pressure control, it really was not possible to reactively sputter Al_2O_3 at high deposition rates in a practical way. A portion of the hysteresis loop for the reactive sputtering of aluminum in

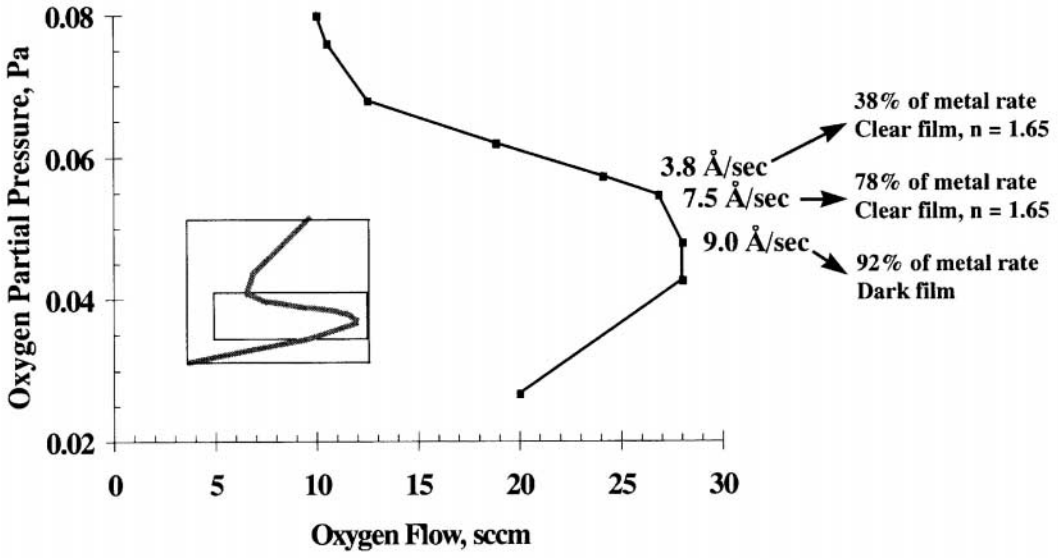

Figure 8. Nose region of the hysteresis curve for the reactive sputtering of aluminum in an argon/oxygen atmosphere. Full curve is shown in the inset in the lower left corner of the diagram.

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