SVC Topics



Donald M. Mattox, Technical Director • Society of Vacuum Coaters 71 Pinon Hill Place N.E. • Alburquerque, NM 87122 505/856-7188 • FAX: 505/856-6716 • www.svc.org

Reactive Sputter Deposition

In reactive sputter deposition, an elemental material is sputtered and the sputter-deposited film reacts with the gaseous environment or a codeposited chemical species to form a film of a compound material. If the compound material thus formed is electrically conductive, such as most nitrides and carbides and some oxides, the sputtering configurations are rather straightforward. A common configuration for reactive sputter deposition uses a single planar magnetron sputtering source as shown in Fig. 1a, though other configurations such as opposing planar magnetrons. Rotatable cylindrical magnetrons and post cathode magnetrons are also used for reactive sputter deposition.

One problem with reactive sputter deposition is the control of the reactive gas, such that there will be enough reactive gas to form the compound film but not too much which would react excessively with the sputtering target surface ("poisoning"). The formation of a compound surface on the target surface greatly reduces the sputtering rate. An advantage of the planar magnetron sputtering cathode is that the surface is aggressively sputtered over a portion of the surface (the "racetrack"), thereby reducing the rate of poisoning in that area. The partial pressure of the reactive gas in the system can be monitored using a differentially pumped mass spectrometer, or by optical emission from the plasma. The monitor output is used to give real-time control of the reactive and inert gas flows.

Figure 2 shows the reactive gas flow as a function of the partial pressure of the reactive gas for the reactive sputter deposition of Ti-N (electrically conductive nitride) and Al-O (electrically insulating oxide)¹



Fig. 1—Planar magnetron reactive sputter deposition systems. 1a) Conventional DC diode system, 1b) "Hidden anode" system, 1c) Mid-frequency dual magnetron AC system, 1d) Alternate metal deposition and oxygen ion bombardment system.

using a planar magnetron sputtering target. The hysteresis effect of increasing, then decreasing, the flow is due to poisoning of the "racetrack" sputtering area of the planar magnetron at high partial pressures. The details of the partial pressure-mass flow relationship depend on a number of factors. Reactive deposition should be done in the mass flow region where the partial pressure begins to raise rapidly. The difference in sputtering rate between the "metalmode" (no reactive gas) to the "poisoned mode" (target being completely poisoned) can be a factor of 10 to 20.



Fig. 2—Typical partial pressure-controlled hysteresis curves for reactive sputter deposition 1a) Titanium nitride, 2b) Aluminum oxide.

Reaction Rate

In reactive deposition, the depositing material must react rapidly or it will be buried by subsequent depositing material. Therefore, chemical reaction rate is an important consideration. The reaction rate depends on the availability of the reactant gas, the chemical reactivity of the species involved, temperature, and in some cases, concurrent ion or electron bombardment during deposition. At 1 mTorr partial pressure, there will be about 10¹⁷ reactive particles (~100 monolayer equivalent) impinging on the depositing film surface per second.

Reactive gases can be chemically "activated" in the plasma by dissociation, excitation, ionization or the formation of a new species, such as forming O_3 in an oxygen plasma. This activation increases the reaction probability. Reactive species, particularly if they have a low reactivity, may be adsorbed on the surface without reacting with the depositing atoms. These unreacted species may then be buried in growing film. Electron and ion bombardment can enhance the reactivity of these adsorbed species. Ions of the reactive gas can be accelerated to a high kinetic energy, and this has been shown to increase the reaction probability. Concurrent ion bombardment of the growing film also densifies the deposited coating ("atomic peening") and can preferentially desorb unreacted species.

In reactive sputter deposition of electrically insulating materials of high dielectric strength, such as many oxides (TiO_2 , Al_2O_3 , SiO_2 , etc) and some nitrides (Si_3N_4), several problems arise. One problem is the

"disappearing anode" effect where the surfaces that act as the anode in the system, such as a floating electrode or the chamber walls (as shown in Fig. 1a) becomes progressively coated with the insulating material. This causes changes in the impedance of the plasma and plasma instabilities.

Hidden Anode

The disappearing anode problem can be alleviated by using an anode that is shielded from deposition ("hidden anode"), as shown in Fig, 1b.² Another technique is to use dual magnetron electrodes that alternately act as anodes and sputtering cathodes as shown in Fig. 1c. This configuration is called "mid-frequency dual cathode AC sputtering." ^{3,4} The two electrodes are driven by a symmetric AC voltage (square or sinusoidal) operating in the range of 50 to 250 kHz. By sputter-cleaning a portion of each electrode during the sputtering half-cycle, a clean metal anode is available for the second half-cycle.

Another problem is arcing on the surface of the sputtering target. Arcing in a sputtering system can occur for a number of reasons, including: flaking and shorting by deposited film material, thermoelectron emission from heated oxide material, and charge buildup due to ion bombardment of dielectric surfaces. Sputtering power supplies must be able to handle the arcing by robust construction and arc suppression. In reactive arc suppression, the arc is detected by the increased current flow or the decreased voltage associated with an arc. On detection, the power supply shuts off the voltage or possibly responds with a voltage of reverse polarity. To limit the energy in the arc, the capacitance and inductance of the circuit should be minimized to reduce the stored energy.

Where the sputtering target is not being aggressively eroded over the whole surface, such as in planar magnetron sputtering, a portion of the target surface can be "poisoned" by reaction with the reactive gaseous environment to form an electrically insulating area on the target surface. Positive charge sites develop on these surfaces as a result of positive ion bombardment and secondary electron emission. The rate of charge buildup on these surfaces depends on the ion flux, secondary electron emission coefficient from ion bombardment (0.1 or so per ion), and charge leakage across the surface and through the film. As the surface positive charge builds up, the positive ion bombardment decreases in energy. If the positive charge buildup is high enough, arcing can occur across the surface or through the film. This arcing can eject molten or solid particles that affect the properties of the depositing film.

Arcing on the sputtering target surface (or on the depositing film if bias deposition is used) can be minimized by periodically neutralizing (discharging) all or a portion of the positive charge buildup. This can be done using pulse power on the cathode. The pulse power has a waveform with a periodic "off-time (zero voltage or positive polarity) segment that allows electrons from the plasma to neutralize the surface charge buildup. The pulse power is usually in the form of a pulsed (unipolar) DC or asymmetric AC. The off-time need only be very short (few microseconds), because electrons from the plasma will rapidly move to neutralize any excessive surface charge buildup. The "mid-frequency dual cathode AC sputtering" configuration of Fig. 1c is one such pulse power sputtering configuration.

Other Configurations

There are other reactive sputter deposition configurations that do not have the same arcing problems on the target as the single cathode continuous DC planar magnetron.* A magnetron system where the whole of the target surface is being sputtered, such as post cathode magnetron or a rotatable cylindrical cathode, limits the target area that can be poisoned. Another technique uses periodic sputter deposition and reactive particle bombardment in separate regions of the vacuum chamber, as shown in Fig. 1d.⁵ The sputtering target is "blanketed" by the inert sputtering gas. This configuration has the advantage that the deposition rate is the sputtering rate of the planar magnetron operating in the "metalmode." When reactively sputterdepositing weakly bonded oxides, such as ZnO, PbO, SnO₂, cathode poisoning may be minimized by the addition of hydrogen to the sputtering gas. Hydrogen ion bombardment of the metal oxide will reduce it to the metallic state.

Generally, the sputtering gas

consists of both a reactive species and an inert species (argon). This is because the reactive species generally has a low mass (N = 14 amu, O = 16amu) while argon gas has a higher mass (40 amu), and is therefore more efficient for sputtering. The ratio of the gases can be an important process parameter. When using large or long sputtering targets, a problem may be encountered in providing a uniform flow of activated reactive gas to the depositing film. Therefore, the gas manifold configuration can be important in the design of the reactive sputter deposition system. One way of minimizing the problem of reactive gas distribution is to sputter the compound material that is to be deposited. For example, if the sputtering target is indium-tinoxide (ITO), only a relatively small amount of reactive gas (oxygen) needs to be used in the sputtering gas to make up for oxygen loss during the sputter deposition of ITO. This type of reactive sputter deposition can be called quasireactive sputter deposition.

In reactive sputter deposition, a codeposited condensable species, such as carbon or boron, can be obtained by the decomposition of a chemical vapor precursor species, (i.e. low pressure plasma enhanced chemical vapor deposition (LP-PECVD). Such a process can be used to deposit carbides (TiC) and borides (TiB_2) . In addition, a gaseous reactive species can also be used. Such a hybrid deposition process is used to deposit carbonitrides (TiCN). In such hybrid deposition processes, the codeposited materials may not react or only partially react. Reaction can be enhanced by heating or concurrent ion bombardment during deposition. Obtaining reproducible elemental, chemical and phase compositions in such hybrid deposition processes can be quite a challenge compared to gaseous reactive deposition. Decomposing chemical vapor precursors can create gas phase nucleated ultrafine particles that affect the vacuum system cleanliness and pump maintenance. P&SF

* It should be noted that ion beam assisted deposition (IBAD) in vacuum using thermal evaporation and an oxygen ion "gun" has been used to deposit high-quality oxide films at high rates over small areas since the early 1980s.

References

- W.D. Sproul, M.E. Graham, M.S. Wong, S. Lopez, D. Li and R.A. Scholl, "Reactive Direct Current Magnetron Sputtering of Aluminum Oxide Coatings," *J Vac Sci Technol* A13(3) 1188 (1995).
- 2. P. Frach, U. Heisig, Chr. Gottfreied and H. Walde, "Aspects and Results of Long-term Stable Deposition of Al2O3 With High Rate Pulsed Reactive Magnetron Sputtering," *Surf Coat Technology*, **59**, 177 (1993).
- 3. G. Este and W.D. Westwood, "A Quasi-direct-current Sputtering Technique for the Deposition of Dielectrics at Enhanced Eates," *J Vac Sci Technol* A6(3) 1845 (1988).
- 4. M. Schrerer, J. Schmitt, R. Latz and M. Schanz, "Reactive Alternating Current Magnetron Sputtering of Dielectric Layers," *J Vac Sci Technol* **A10**(4) 1772 (1992).
- J.W. Seezer, P.M. LeFebvre, B.P. Hichwa, J.P. Lehan, S.F. Rowlands and T.H. Allen, "Metal-Mode Reactive Sputtering: A New Way to Make Thin Film Products," p. 229, Proc. of the 35th Annual SVC Technical Conf. (1992).