MATERION

TECHNICAL PAPER

OXIDES AND NITRIDES OF ALUMINUM

Applications and Deposition Processes

Author: Samuel Pellicori
Materion Coating Materials News

This article will compare the properties, applications and deposition processes of films of the Oxygen and Nitrogen compounds of Aluminum; specifically Aluminum Nitride, AlN, and Aluminum Oxide, Al_2O_3 or Alumina. Although they are neighbors on the periodic table of elements, oxide and nitride compounds of various metals exhibit different physical properties and therefore are used to satisfy different applications. While Alumina is found naturally as the material Corundum, AlN does not occur naturally but must be artificially grown.

Comparison of Properties

The common oxide compounds of Aluminum, Tantala, Silica, Titania and Alumina are transparent between near-UV and Mid-IR wavelengths, with Alumina transmission reaching ~250 nm. For that reason, these compounds are often used in thin-film optical coatings. Alumina optical films provide some degree of protection against abrasive wear and chemical reaction. However, they are never as hard as crystalline sapphire, because the density and morphology of the films are not of the same form.
The common nitride compounds of Aluminum Nitride (AlN) and Silicon Nitride (SiN) are transparent at wavelengths longer than mid-visible wavelengths and produce hard coating layers. Compounds of transition metals to form Titanium Nitride (TiN), Chromium Nitride (CrN) and others are not transparent, but find application as tribological and wear resistant coatings such as on tools, decorative surfaces, and high-temperature applications.

Applications

Aluminum Oxide films are used in optical coatings several ways: as an intermediate index material, as a protective overcoat for aluminum and silver mirror films, and in thick layers as a barrier to salt, steam, and other corrosive agents. Thick Aluminum Nitride films are used as piezoelectric transducers. Depending on the crystal growth axis, the piezoelectric (PZ) properties differ with orientation **[1]**. Thick layers of both Zinc Oxide (ZnO) and AlN have desirable PZ properties; each suitable for a specialized application. Orientation of the film layer along the c-axis produces the largest PZ effect, therefore crystalline growth morphology and axis orientation must be appropriately controlled. The ability to sputter thick (>20 µm) layers of oriented AlN with superior PZ properties provides an alternative to ZnO. Martin **[1]** mentions two advantages: AlN processing is compatible with silicon semiconductor technology processes, and AlN tends to possess and maintain higher conductivity and thus higher efficiency over a range of driver frequencies.

Piezoelectric devices are used to produce small mechanical motions, either linear or angular, as applied to micro-mechanical motion (MEMS) actuation using electrical stimulation. PZ devices can be driven at high frequencies as transducers. Conversely, small currents can be generated by mechanical stressing a PZ material. **Figure 1** illustrates the configuration that can be used for either application.

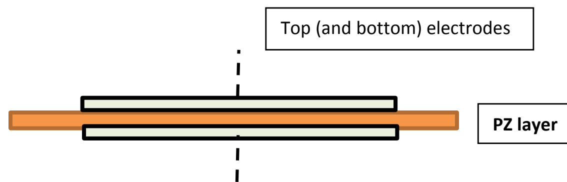

Figure 1. General configuration of a PZ actuator/transducer. Electrical stimulation causes mechanical motion; mechanical stress causes electrical current generation. The electrodes are metal (Al/AlN/Al) or they can be transparent conductors such as ITO or AZO.

An application of the PZ effect uses AlN in transducers operating as high as 100 MHz in ultrasonic modulators. Such transducers are found in ultrasound sensors, MEMS actuators, SAW drivers (surface acoustic wave), RF filters and resonators, bio-sensors and others. The AlN PZ layer for these applications needs to be 10's of µm thick and of high quality in terms of crystal orientation. This greater thickness requires tens of hours of deposition time by typical methods such as sputtering.

Deposition Processes

Al_2O_3 can be deposited by E-beam evaporation. Higher quality film layers are deposited when aluminum metal is used as the source material and oxidized to Al_2O_3 with the aid of energetic ions, instead of using alumina as the starting material. Aluminum metal evaporates at a higher rate than Al_2O_3 and the density of particulate film inclusions created is very low by comparison. This property increases the laser damage threshold (LDT) by a large amount. High rates of deposition of Al_2O_3 by E-beam can be obtained, but only substrate materials such as glass can tolerate the high thermal load that accompanies the IAD E-beam process.

AlN cannot be deposited by thermal techniques, but other processes such as pulsed laser, CVD, dual ion-beam sputtering, and MBE have been used. However, deposition efficiency, equipment costs, and general ease-of-process considerations favor sputter deposition for AlN and Al_2O_3 layers. Pulsed DC magnetron sputtering has also been successfully employed **[2]**.

In a previous issue of *Coating Materials News*, we presented a "Tutorial on Sputter Deposition" in which the essential elements of a sputtering system were described **[3]**. Here we expand on the basic physics of the reactive sputtering process, especially as they pertain to AlN and Al_2O_3 layer reactive deposition.

As shown in **Figure 2**, the essential physical components are the metal target (cathode) and a substrate to be coated (at anode potential). A discharge voltage established by the electrical potential difference between target and substrate produces a specific power density at the substrate. This is one of the prime variables in the reactive process. An electron and ion plasma is established in the space between target and substrate in a working gas such as Argon. The cathode or target is backed by a magnet array whose magnetic field confines and concentrates electrons near the target surface. Within the plasma region, electrons ionize the working gas Argon and the reactive gas, O_2 or N. The heavier Ar ions created in the plasma are accelerated to impact the target and cause atoms of the metal to be mechanically sputtered from the target surface by momentum transfer.

Depending on the total gas pressure, which determines the mean free path and influences reaction rates, the sputtered metal atoms are attracted to the substrate surface with a kinetic energy of 1-10 eV where they react with the ionized reactive gas and grow an oxide or nitride film layer. The deposition rate of the growing film is determined by the energy density at the cathode surface (discharge voltage), the flow rate of the reactive gas and the chamber total pressure.

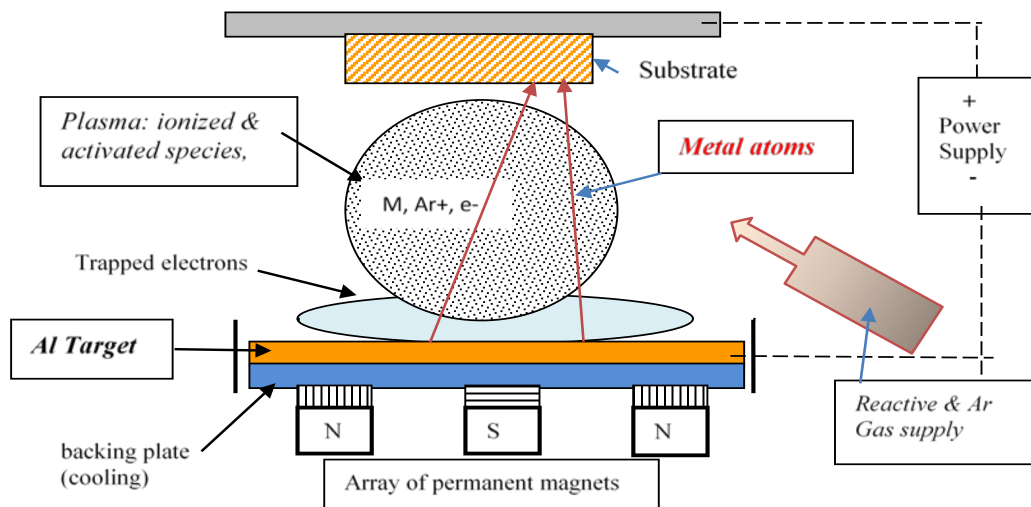

Figure 2. Components of a reactive DC magnetron sputtering system for depositing Al_2O_3 or AlN film layers.

Reactive sputtering of an Al metal target is the preferred process for the deposition of AlN and Al_2O_3. Target properties such as small grain size, high packing density, and high compositional purity are the prime characteristics that relate to the film quality required in the ultimate application of the layer. Some semiconductor devices require the highest level of purity (five-9s), while many optical applications (with the exception of high LDT coatings) can tolerate three or four-9s purity.

In composing the compound, Oxygen or Nitrogen gas is admitted at a proportional flow rate with the working gas Argon. While targets composed of the compounds can be sputtered, RF power is required for this because these targets are not conductive, and poor thermal conductivity often results in cracked targets. Reactive DC magnetron sputtering is capable of producing at high rates under controlled operating conditions. The characteristic phenomenon is dominated by the growth of an oxide or nitride insulating layer on the metal target surface which lowers the deposition rate and related parameters. The rate of the so-called target "poisoning" is greater with oxides, but tight control of power, discharge voltage, and reactive gas flow is required for both AlN and Al_2O_3 film growth. Next we will examine the process kinetics in greater detail.

If conditions are proper, Aluminum atoms are sputtered from the target and a reaction occurs on the substrate surface to build a film layer at an acceptable rate. The insulating film growing on the target surface competes with consumption of reactive gas and the strength of the discharge voltage that generates the plasma and determines the deposition rate.

This "target poisoning" film consumes the available oxygen or nitrogen gas and reduces the discharge voltage and deposition rate. To restore the target surface to metal, the reactive gas low rate must be sufficiently reduced. Unfortunately, the transition point between metallic and oxidized (nitride) surface is unstable and difficult to control. The build-up of insulating surfaces occurs not only on the target, but also on all surfaces inside the chamber. As electrical charge collects on the insulators, arcing can occur and disrupt the process and produce particulates and other defects on the substrate. Arc-suppressing power supplies are available.

Another approach to preventing target poisoning is to employ two targets whose polarity is rapidly alternating so when one target is sputtered, the other is simultaneously cleaned of the oxide (nitride) layer. High-frequency pulsed DC magnetron sputtering with arc suppression is another technique that is reliably used for oxide compound deposition. The rate kinetics of the reactive process, which applies to the sputtering of compounds films from any metal target not solely to aluminum, illustrated in **Figure 3.**

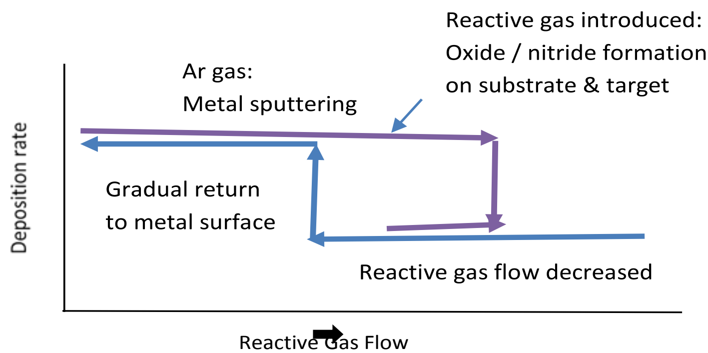

Figure 3. Rate kinetics as influenced by reactive and working gas flow rates. Stabilizing the reactive process at the arrow position is desired, but requires special control of variables.

As the working gas Ar is introduced, metal atoms are sputtered. When the reactive gas is introduced, the rate decreases and the compound deposits on the substrate and all chamber surfaces. This corner of the right-trending curve is the critical point at which a high rate of the compound is deposited. It is desirable to operate at or near this corner. However, as the reactive gas is consumed in the reaction to compose the compound, the rate lowers because the target surface is also oxidized or nitrided and becomes insulating. Restoration to pure metal only occurs when the reacting gas flow is reduced and working gas can etch the compound from the target surface to expose pure metal. At the same critical point, the discharge voltage that maintains the plasma decreases for oxide films, and this works against a high rate. The discharge voltage increases for nitride films.

Control of the process rate and film stoichiometry can be instrumented with techniques that produce stability and repeatability. Control of reactive gas flow as a function of target voltage in a control loop is one method that works well for AlN, but not as well for oxide compounds **[4]**. The most effective method is to provide reactive gas flow feedback control by monitoring the concentration of the ionized species of the reacting gas. Optical sensing of the strength of a spectral emission line of the reactive element (O_2 or N) activates a gas flow valve at high speeds (such as a PZ) valve.

Conclusion

Some of the applications and deposition processes for building AlN devices were discussed. Also covered were the sputter process involved and the differences between alumina and AlN films. Materion is an industry-leader in high purity source materials for sputter deposition and can assist with questions about appropriate compounds for a range of applications.

References

1. Martin, Peter M., "Mechanically Active Thin Film Materials: Piezoelectric Thin Films," Vacuum Technology and Coatings, June 2015, 6-13.
2. Choudhary,R.K., P. Mishra, A. Biswas, and A. C. Bidaye, " Structural and Optical Properties of Aluminum Nitride Thin Films Deposited by Pulsed DC Magnetron Sputtering," ISRN Materials Science, V2013 (2013), Article ID 759462.
3. Coating Materials News, V 21, Issue 2, Sept 2011, "Tutorial on Sputter Deposition"
4. Glocker,D. "AC Reactive Sputtering with Inverted Cylindrical Magnetrons," Annual Society of Vacuum Coaters Technology Proceedings, April 2000, 81-85.

Principal Contributor: Samuel Pellicori
Pellicori Optical Consulting, Santa Barbara, CA
Phone: 805.682.1922, Email: pellopt@cox.net

Material Advanced Materials Group is a global supplier of premier specialty materials and services. Our offerings include precious and non-precious thin film deposition materials, inorganic chemicals and microelectronic packaging products. In addition, we offer related services to meet our customers' requirements for precision parts cleaning, precious and valuable metal reclamation and R&D. We support diverse industries including LED, semiconductor, data storage, optical coatings, large area glass and aerospace.