SVC Topics



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A Concise History of Vacuum Coating Technology Part 2b: 1940-1975

Vacuum Vaporization The equilibrium vapor pressure of materials and the rate of thermal evaporation from a hot surface were studied by Langmuir (1913) and Knudsen (1915). In 1956, Knacke and Stranski reviewed the various methods for measuring the equilibrium vapor pressure of materials. In 1962, Hoenig and Cook published a comprehensive tabulation of equilibrium vapor pressures.

The oriented growth films on crystalline substrates by vacuum

deposition (epitaxy) has been known since the discovery of electron diffraction. Early work on epitaxy was reviewed by Pashley (1956). Molecular beam epitaxy (MBE) is a very carefully controlled thermalevaporation-deposition technique for depositing single-crystal films on single-crystal substrates (Chang, Eski, Howard & Ludeke, 1973). Commercial use of MBE for the controlled growth of III-V epitaxial semiconductor layers was first developed by Cho and Arthur (1975), derived from

earlier work by Gunther (1958).

Various types of filaments, boats and crucibles were developed in the early part of this period. Silicon monoxide was the most frequently used evaporated dielectric for thin film capacitors, optical coatings and protective topcoats. Drumheller (1961) designed a baffle-type ("chimney") evaporation source for silicon monoxide to avoid "spits."

In 1940, Ruhle introduced the heating and evaporation of materials from a crucible using an accelerated



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SUR/FIN® 2000 ... Booth #1134. Free Details: Circle 160 on reader service card or visit www.aesf.org/psf-qwiklynx.htm. electron beam, but not much development was done on this technology until the early 1950s. By 1955, ebeam evaporation using unfocused work-accelerated electron beams had become rather commonplace. In 1954, Pierce described the linear long-focus, electron-beam gun, which was developed into very high-wattage configurations (Denton & Greene, 1963). A problem with this arrangement for film deposition was coating of the high-voltage insulators. Several bent-beam electron sources were being developed (Holland [patent], 1951; Denton & Greene, 1963). In 1961, the 270-degree bent-beam electron beam evaporation source eliminated this problem and became the standard e-beam evaporationsource configuration. In 1963, Morley described the use of a hollow cathode discharge (HCD) electron source for vacuum melting and evaporation. In 1971, Wan, Chambers and Carmichael described how a highvoltage, hot-filament, electron-beam gun could be used to evaporate material into a plasma for ion plating.

Because of the difficulty in thermal vaporization of alloys of materials

with differing vapor pressures and the slowness of sputter deposition, various techniques of flash evaporation were developed for depositing films of alloy materials. In flash evaporation, small amounts of material are completely evaporated periodically. This can be accomplished by dropping pellets (Harris & Siegel, 1948) or powder (vibratory feed) on a hot surface or by tapping the tip of a wire on a hot surface. Smith and Turner (1965) demonstrated film deposition in vacuum using a high-energy pulsed laser for flash evaporation ("laser ablation") from a spot on a surface. This technique was later called pulsed laser deposition (PLD), and was used for deposition of good-quality high-T superconductor and ferroelectric films in the mid-1980s.

In some applications, large amounts of material could be evaporated from multiple sources. In other applications, large amounts of material needed to be vaporized from a specific point. This led to the development of thermal-evaporation sources, which could be continuously replenished ("feeding" sources). These included the wire-fed and rodfed evaporation sources, as well as pellet-drop systems. An interesting application of the rod-fed e-beam evaporation system was the deposition of complex alloys (Santala & Adams, 1970; Nimmagadda, Raghuram & Bunshah, 1972). In this application, the e-beam is focused on the center of the rod such that the molten pool is contained in a "crucible" of the rod material. If the volume of the molten material is maintained at a constant rate, the pool will reach an equilibrium composition different from the composition of the rod. However, the vaporized material will have a composition that is the same as that of the rod. This technique was used to coat turbine blades for aircraft engines with MCrAlY alloys before sputter deposition techniques were developed.

Before 1950, there were two theories of sputtering. One, the "hot spot" theory, invoked thermal evaporation from a molten hot spot on the surface. The second, the "momentum transfer" theory, invoked physical collisions between atoms. The "hotspot" theory was discredited by the observations of a crystallographic dependence on sputtering yield (Henschke, 1957; Anderson & Wehner, 1960) of a "threshold energy" for sputtering (Stuart & Wehner, 1962), and that the vaporized atoms had greater than thermal energy. A number of investigators determined many of the sputtering yields by measurement or calculation (Almen & Bruce, 1961; Laegreid & Wehner, 1961; Sigmund, 1969). In 1942, Fetz observed that the sputtering yield was a function of the angle of incidence of the bombarding ion, and this was confirmed in the early 1960s (Almen & Bruce, 1961; Cheney & Pitkin, 1965). Wehner studied the basics of the sputtering process and determined sputtering yield values under contract to NASA, which was concerned about the effect of sputtering on the surface of the moon. Much of Wehners' early work used mercury ions for the sputtering particle. Colligon (1961) and Wehner (1962) have discussed the details of the historical development of sputtering. In 1960, Davies, Friesen and McIntyre made the first accurate

measurements of the range of highenergy ions in solids and laid the foundation for ion implantation processing and Rutherford backscattering spectrometry (RBS).

The earliest report on radio frequency (rf) sputtering of dielectric materials was by Robertson and Clapp in 1933. In 1962, Anderson, Mayer and Wehner used rf sputtering to clean glass vacuum windows. In 1963, Butler and Kino discussed the origin of the self-bias on an rf-driven insulating electrode. In 1966, Davidse and Maissel used rf sputtering from a dielectric sputtering target to sputterdeposit dielectric materials. A disadvantage of rf sputtering of dielectrics is that most dielectrics are highly susceptible to thermal shock and easily cracked. This means the power input to the target must be kept low, and that means the sputtering rate is generally very low. An exception is SiO₂, which has a low thermal coefficient of expansion. Radio frequency sputtering has the added advantage that at high rf frequencies, the radiated power induces potentials on surfaces

throughout the deposition chamber and reduces arcing in the chamber. The rf reactive sputter deposition of Al_2O_3 from an aluminum cathode was reported by Frieser, Potter and Smith in 1965. In 1967, Vratny superimposed DC and rf for the alternate sputter deposition of tantalum and reactive sputter deposition of Ta₂O₃ from a tantalum target.

Before 1970, the most common sputtering configuration used a largearea DC diode target. Because of the energy losses resulting from physical ("thermalization") and charge exchange collisions (van der Slice, 1963), as accelerating ions move through the rather dense gas needed to sustain the gas discharge, high voltages were used—but the average bombarding energy and the sputtering rate were low. An advantage of the planar cathode was that a large area of uniform erosion (and deposition) could be attained.

In the late 1930s, the electron-trap called the "Penning effect" was used to enhance plasmas used for sputtering from cylindrical-hollow (inverted) magnetrons (Penning 1936) and cylindrical-post magnetrons (Penning & Mobius, 1940). In the Penning discharge, a combination of electric and magnetic fields is used to confine the plasma near the surface of the sputtering target. By having an appropriate magnetic field configuration, the electrons circulated in a closed path near the surface, giving increased ionization and a short acceleration distance to the target. This allowed sputtering to be performed at lower pressures and lower voltages, and at a higher rate than with non-magnetic DC sputtering. Various surface magnetron configurations were designed in the late 1960s and early 1970s (Mullaly [hemispherica], 1969; Clarke [S-gun & sputter-gun], 1971; Chapin [planar], 1974; Penfold & Thornton [post], 1975). Major advantages of some of these sputtering sources were that they could provide a long-lived, highrate, large-area, low-temperature vaporization source. With their new performance characteristics, sputtering sources began to replace thermal evaporation in some applications and enabled new applications to develop.

A disadvantage of the magnetron sources was that the plasma was confined to a small volume near the surface of the sputtering target and was therefore not available for "activation" of reactive gases near the substrate. This presented problems in the reactive deposition of compound films, such as nitrides. This disadvantage could be overcome by the use of auxiliary plasma sources. These plasmas could be formed by providing rf as well as DC on the sputtering target (Vratny 1967; White 1972) or by having an auxiliary plasma, often magnetically confined, near the substrate. The use of such auxiliary plasmas was cumbersome, and use decreased with the advent of unbalanced (UB) magnetron sources (Windows & Savvides, 1986). The unbalanced magnetron allows some electrons to escape from the confining **E X B** field and creates plasma in a region away from the target surface. If the escaping magnetic field can be linked to other UB magnetron sources, the plasma-generation region can be made very large.

The planar sputtering configuration

became the most popular magnetron design. A disadvantage of the planar magnetron sources is that they generally have a defined erosion pattern that is usually in the form of a circle or elongated "racetrack." This gives non-uniform erosion over the target surface, low target material utilization and a non-uniform deposition pattern. In order to obtain uniform deposition on a substrate, it is typically necessary to fixture and move the substrate in a specific manner or to have a moving magnetic field in the target.

When bombarding a surface, some of the bombarding ions are neutralized and reflected from the surface. If the gas pressure is low, these highenergy neutrals can travel appreciable distances before they are "thermalized" by collisions with gas molecules. The reflection of the highenergy bombarding particles from a sputtering target was studied by Jepsen (1968) and by Vaumoron and DeBiasio (1970). Generally, sputtering is performed from a cold, solid surface using gaseous (usually argon) bombarding ions. In 1970, Kreutenat and Gesick showed that in sputtering from a liquid metal target, which was also evaporating, a plasma could be sustained using only the metal vapor, then self-sputtering by metal ions would occur. In 1972, Weissmantel used an ion beam source for sputtering and sputter deposition in a good vacuum.

In 1954, Bradley used vacuum arc vaporization for the deposition of carbon films for TEM replication. Refractory metal film formation by arc vaporization in vacuum was reported in 1962 (Luca, Vail, Stewart & Owen). In the early 1970s, several arc vaporization sources were patented (Snaper, 1971; Sablev, 1974) but the commercial availability of arc vaporization sources for film deposition in the U.S. really began in about 1980 (MultiArc Corp.).

Deposition Processes

If the gas density (vacuum) is sufficiently low, atoms vaporized from solid or liquid surfaces by evaporation, sputtering or arcing condense on surfaces in the vacuum system, atom by atom. If the gas pressure is too high, multi-body collisions cause gas-phase nucleation and the formation of clusters of atoms or "soot." The soot condenses on surfaces, giving a low-density coating.

Film deposition is the condensation of atoms or molecules on a substrate surface. The origin of the condensing species is often unimportant. Generally what is important in nonreactive deposition is the chemical interaction between the depositing species and the surface, the temperature of the surface, the kinetic energy of the of the depositing particles, the angle-ofincidence, the flux distribution of the depositing species and, sometimes, the rate of deposition. Added to this, in some cases, are external sources of energy and momentum, such as concurrent bombardment with highenergy atomic-size particles. In reactive deposition, the chemical reactivity and availability of the reactive species-such as nitrogen, oxygen, and carbon-are important to converting the depositing elemental coating material into a compound material.

Until the mid-1960s, the principal PVD deposition variables were substrate temperature, deposition rate, angle-of-incidence of the depositing atoms and, possibly, gas pressure and composition. In 1963, Mattox introduced the ion plating process (patented 1967). The ion plating process uses atomic-sized energetic particle bombardment to clean the substrate surface (sputter-clean), maintain a clean surface until the depositing material covers the surface, then to modify the film properties by controlled continuous or periodic bombardment during deposition. The ion bombardment during nucleation and film growth modifies the surface, introduces heat directly into the nearsurface region without having to heat the bulk of the substrate and, by collision processes, causes densification of the film. Ion plating is also called ion-assisted deposition (IAD) and ion vapor deposition (IVD-[aerospace industry]). When using a chemical vapor precursor, it is sometimes called chemical ion plating, which is a low-pressure form of plasma-enhanced chemical vapor

deposition (PECVD). In 1971, Culbertson used chemical ion plating to coat carbon on electron tube grids to reduce secondary electron emission.

Using the ion plating process, it was shown that film adhesion and surface coverage could be improved in many cases. It was later shown that the bombardment will densify and refine the film morphology for both conducting (Mattox & Kominiak, 1972; Patten & McClanahan, 1973; Bunshah & Juntz, 1972) and nonconducting (Mattox & Kominiak, 1973) deposits. Ion bombardment can introduce high compressive stresses (Bland, Kominiak & Mattox, 1974; Hoffman & Thornton, 1977). These effects are similar to that achieved by shot peening, so the ion bombardment was called "atomic peening" (Blackman, 1971; Hoffman & Thornton, 1977).

In the ion plating process, initial bombardment was attained by accelerating ions from a plasma to the substrate/growing film, which was the cathode of a DC diode discharge. The accelerated ions and high-energy charge-exchange neutrals (van der Slice, 1963) provided a spectrum of bombarding energies due to the relatively high gas pressures needed to sustain a DC diode gas discharge. With the advent of magnetron sputtering, which can be done at lower gas pressures than nonmagnetron discharges, bombardment can also come from high-energy neutrals reflected from the sputtering cathode. In 1968, Vossen and O'Neill used an rf bias ("rf ion plating") on a dielectric substrate (silicon) to allow ion bombardment of the growing film (aluminum) on a dielectric material. Davy and Havak (1974) used an rf bias on the substrate during deposition of non-metallic films by evaporation.

Film deposition using a pure beam of high-energy carbon ions ("film ions") was used by Aisenberg and Chabot in 1973 to form pure carbon films. Carbon films formed under bombardment conditions were later shown to have diamond-like properties and became one method of forming diamond-like carbon (DLC) films. In 1974, Chin and Esver reported the reactive ion plating of Si₃N₄ from a silicon target on thermoelectric materials. In 1978, Gautherin and Weissmantel used an ion "gun" to bombard depositing films in good vacuum ("high-vacuum ion plating").

The use of an AC potential for periodically bombarding the depositing film, as well as the sputtering target, was reported in 1962 as a means for improving the properties of a sputter-deposited magnetic film material. This periodic bombardment of the depositing film was later called "alternating ion plating" (Schiller, Heisig & Goedicke, 1975). In 1975, Murayama, as well as Chin and Elsner, reported reactive ion plating using an rf coil above the evaporation source to provide a dense plasma and some post-ionization of the evaporated material.

Bombardment prior to and during deposition can result in gas incorporation into the substrate surface (Chleck & Maehl, 1963; Kornelsen, 1972) under some conditions. Bombardment during deposition can result in gas incorporation in the film (Guilder 1964; Winters & Kay, 1967; Mattox & Kominiak, 1971; Cuomo & Gambino, 1977) that can lead to void formation. Gas incorporation can give problems with adhesion and film porosity. Film stress and gas incorporation can be controlled with proper coating parameters. Early work on ion plating was reviewed by Mattox in 1973.

Thermal chemical vapor deposition (CVD), which used the thermal decomposition or hydrogen reduction of a chemical vapor precursor(s) to form a coating, is normally performed at atmospheric pressure (APCVD). In some cases, sub-atmospheric pressures (SA-CVD) or low pressures (LP-CVD) are used to control gas flow, temperature distribution or gas concentrations. Thermal CVD generally requires a high temperature, which restricts its application. However, it was used very early in the fabrication of semiconductor devices, particularly for forming doped epitaxial silicon layers (vapor phase epitaxy) and encapsulation. Plasmas can be used to enhance the decomposition kinetics and allow deposition at lower temperatures-typically 200-300° C-than thermal CVD and still obtain the same quality of material. In 1974, Reinberg introduced the lowpressure (100 mTorr to 2 Torr), rfdriven, parallel-plate, plasmaenhanced CVD (PECVD) reactor, which then found wide use in depositing coatings of silicon, compounds and glassy materials in the semiconductor-device industry.

As early as 1963, attempts were made to "write" thin-film circuitry using ion beams of metallic materials (Kaspaul & Kaspaul) without much success. In 1973, Berg and Mattox reported writing tungsten metal-lines using a laser for local heating and low-pressure WCl₆ as a CVD precursor. In the early 1970s, Takagi reported the "ionized cluster beam" (ICB) deposition process (Takagi, Yamada, Kumnori & Kobiyama, 1972; Takagi, Yamada & Sasaki, 1975). In the ICB process, clusters of atoms (1,000 or so) were formed, ionized and accelerated to high energies before deposition. It was later determined that, in many cases, clusters were not formed in the work published and the effects noted were the result of bombardment by atomicsized ions.

(To be continued.) P&SF

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