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# Surface Engineering of Glazing Materials and Structures

# Using Plasma Processes

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**Abstract**
A variety of coatings is commercially produced on a very large scale, including transparent conducting oxides and multi-layer silver-based low-emissivity and solar control coatings. A very brief review of materials and manufacturing process is presented and illustrated by ultrathin silver films and chevron copper films. Understanding the close relation between manufacturing processes and bulk and surface properties of materials is crucial for film growth and self-assembly processes.

## 1. Introduction

Since the first oil crisis in the 1970s, huge savings have been accomplished by reducing heating loads in cool climates and cooling loads in hot climates using spectrally selective, transparent coatings [1-3]. While almost all coatings are static, switchable coatings have been developed with window applications in mind as early as in the 1980s [4]. The technical difficulties have been underestimated to make large area windows with switchable optical properties in economical manner, however pilot products are on the market today.

With advances in coatings technology and the explosive growth of nanotechnology, new concepts are being considered, including patterned or self-assembling structures, graded layers, and new switchable materials. The packing density of coatings and structures can reach from dense (bulk-like) to very porous (foams and "cauliflower") structures. Coatings can be produced by a variety of processes, and here we limited ourselves to plasma and plasma-enhanced processes relevant to glass and web coating.

Over the last years, great advances have been made in plasma processing of materials and in the understanding of structure-property relationships. Materials structures, properties, and processes are connected by a feedback loop. This loop can be utilized to design the process and to control manufacturing within tight tolerances.

## 2. Structure, property, and process relationships

A major advancement in understanding the correlation between structure, properties, and process was achieved with the introduction of structure-zone diagrams, i.e. diagrams describing the microstructure of thin films in terms of process parameters. In 1969, Movchan and Demchishin [5] showed that evaporated films exhibit a porous and columnar structure when deposited at low homologous temperature, while smooth, amorphous or nanocrystalline films are formed at intermediate temperatures, and large-grain crystalline films are typical for high temperatures. Homologous temperature is defined as the ratio of the actual temperature and the melting temperature of the deposited material. Thornton [6] expanded the concept to sputtered films by introducing a third axis to the zone diagram describing the sputter pressure, which is an indirect but practical measure of particle energy. Messier et al. [7] refined the Zone Model by taking into account the enhancement in surface mobility due to ion bombardment. A more detailed understanding of these largely empirical diagrams came with Monte Carlo (MC) and molecular dynamics (MD) calculations where atomic interaction potentials were introduced. For example, Müller [8] showed that the packing density of films can be increased by ion bombardment because the kinetic energy

of arriving ions enabled surface atoms to overcome energy barriers for surface diffusion. Thus kinetic ion energy has a similar effect as high substrate temperature. However, the kinetic energy of ions and elevated substrate temperature are not equivalent, especially when considering the texture of films. While high substrate temperature promotes crystallization and grain growth, high kinetic energy of ions creates atomic collision cascades, ion mixing, ion damage of crystalline structures, and amorphization.

The development of a clear understanding of the relative roles of thermodynamics and kinetics on the growth of films and microstructures is still at the center of modern coatings research. For each deposition process and materials system it is desirable to understand the relation in the trilogy process-microstructure-properties. As the characteristic length scale in films decreases, the relative importance of the individual physical processes during growth changes. Parallel to the increasing complexity of the materials systems, the complexity in modern deposition processes has also increased, and it is critical to establish a correlation between practical "process control knobs" (like pressure) and actual process parameters (like energy distribution functions). A satisfactory film growth model needs to take plasma effects as well as surface and solid state properties into account.

## 3. Plasma Processes

The motivation to proceed with the development of nanostructured materials resides in the capability of creating devices with improved or novel properties, or enhancing the performance of existing components. Introduction of novel materials and structures requires concurrent development of fabrication techniques: plasma processing is highly compatible with glass coating technology, and capable of producing materials engineered at the nanometer scale.

To appreciate the great progress in process development made over the last years, and limiting ourselves to sputtering, the following developments should be recognized:

- Magnetron sputtering: Enhancement of the plasma density at the target by a magnetic field;
- Unbalanced magnetron sputtering: the magnetic field lines are not closed at the target, thus flow to the substrate is enhanced;
- Ionized sputtering: Additional plasma ionization is accomplished by coupling additional power into the plasma, usually by RF fields [9];
- Reactive sputtering: Introduction of reactive gas such as oxygen or nitrogen in the sputter gas mixture, deposition of compound films [10];
- RF sputtering: insulating targets can be used [10];
- Dual or twin magnetron sputtering: Two targets working with alternating current, often at medium frequency, so one of the targets is sputtered (cathode) while the other is anode; in this way the problem of the "disappearing anode" is solved because no insulating film can grow on the anode [11];
- Rotating magnetron sputtering, often with cylindrical cathodes: target utilization is greatly improved;
- Pulsed power sputtering: During pulses, the current (hence power) is increased by orders of magnitude; the degree of ionization and particle energy can be greatly enhanced [12,13].

For selected applications, plasma or plasma-assisted processes other than sputtering are being used. Among them are:

- Ion plating: High current discharge in evaporated material, leading to partial ionization of vapor and allowing substrate bias to be effective; modern variants include *rod cathode arc activated deposition* (RAD) [14], *spotless arc deposition* (SAD) [15], and *hollow-cathode activated deposition* (HAD) [15];
- Pulsed laser deposition: characterized by ablation and ionization of material from any solid target, suitable for synthesis of high-temperature superconductors and other high-value, small-area applications [16];
- Pulsed and DC cathodic arcs: streams of fully ionized plasma from solid conducting cathodes, can operate in vacuum or in gaseous environment, needs filter to remove macroparticles for optical and other high-quality coatings [17];
- Plasma-assisted atomic layer deposition: A special case of chemical vapor

deposition in which species are plasma activated and film growth is self-limiting, i.e. deposition stops when one atomic layer has formed on the substrate.

Pulsed laser deposition, cathodic arc deposition [18,19], ion plating [20], and plasma immersion techniques [21] belong to "energetic condensation," i.e., techniques where a significant fraction of condensing atoms or ions arrive with hyper-thermal kinetic energies (typically 20 eV or higher) [22,23].

## 4. Two selected examples of plasma processes for glass coatings
### 4.1 Ultrathin silver films

High performance low-e and solar control coatings contain at least one but often two or three ultrathin silver layers [3]. The silver layer thickness is a compromise between low sheet resistance (hence low emissivity) and high transmission. It is therefore desirable to have very thin (~10 nm) silver layer that grows in a layer by layer mode (Frank-van der Merve) rather than in the island (Volmer-Weber) mode. The growth mode is a function of interaction energies of substrate and film atoms on one hand, and among film atoms on the other. In the absence of significant kinetic energy of atoms and ions arriving at the surface, the interaction energies and surface temperature would determine the growth mode entirely. However, in a plasma process, especially in case of energetic condensation, the kinetic energy of arriving particles is large and can therefore strongly modify the film growth process.

Fig 1 shows an example when silver is conventionally sputtered and deposited energetically using a filtered cathodic vacuum arc (FCVA) plasma [24]. In-situ measurement of the sheet resistance was done immediately (i.e. within seconds) after film deposition. It was found that, initially, FCVA-deposited films are continuous at a thinner nominal thickness than sputtered silver films. However, the sheet resistance changed on a time scale of minutes, indicating that thermodynamic driving forces are able to change the film even at room temperature. This can be understood considering the contribution of surface energy, which has a relatively larger contribution to the system's energy when the film is very thin.
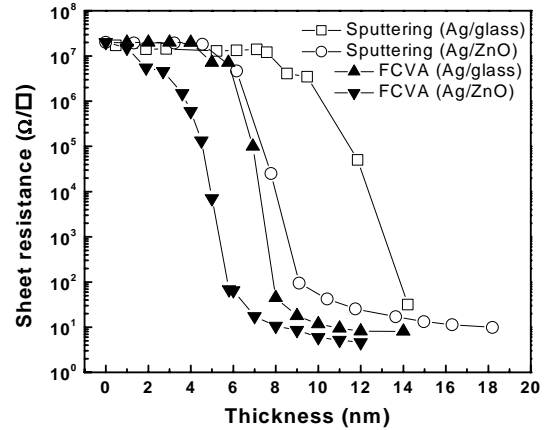


Fig. 1. Sheet resistance as a function of nominal thickness of silver films deposited by magnetron sputtering and by energetic condensation via filtered cathodic vacuum arc (FCVA); for details see [24].
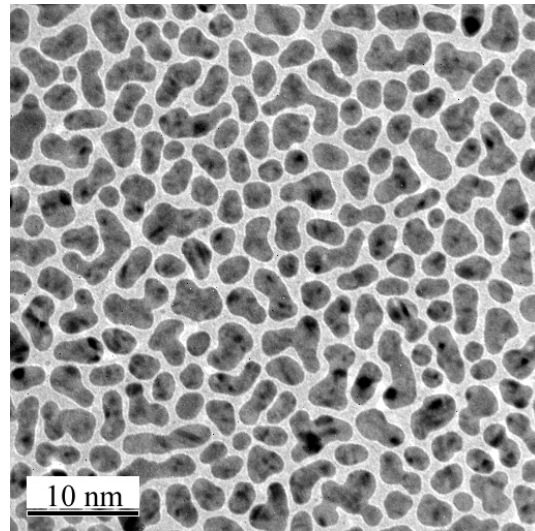


Fig. 2. Silver island on a silicon nitride TEM membrane, deposited by filtered cathodic vacuum arc, with nominal thickness 6 nm.

This point is also illustrated by silver simultaneously deposited on borosilicate glass, ZnO-coated glass, and $Si_3N_4$ membranes used for transmission electron microscopy (TEM). While the low sheet resistance data on ZnO-coated glass indicates a continuous film at 6 nm (nominal), the TEM picture (Fig. 2) shows well-separated silver islands. The difference were likely caused by the different substrate-film interface energies and a higher temperature

of the thin $Si_3N_4$ membrane compared to the glass, which is the result of process heating and minimal heat conduction due to the geometry of the membrane [25].

This example provides a good demonstration of differences that can be expected when films are prepared using energetic and non-energetic deposition processes. The final microstructure is determined by a combination of thermodynamics and kinetics. Kinetically determined growth results in films that are far from equilibrium, and the farther they are, the more sensitive to long term changes ("aging") they are.

Another interesting approach to modify the microstructure of a growing film is to add minute amounts of an element that affects a limiting step in the layer growth process, i.e. an alloying material that can act as surfactants altering surface diffusion. It is now recognized that one important aspect of interface diffusion is the migration of adatoms down surface steps, due to the existence of an energy barrier to step diffusion known as the Ehrlich-Schwoebel (ES) barrier [26,27]. Lowering this energy barrier can lead to increasing the adatom mobility of the films, particularly increasing the rate of migration down on surface steps, and therefore promoting film coalescence at an earlier stage than would otherwise be achieved. Taking advantage of this fact, Huang et al. [28] have used controlled additions of indium to promote a decrease of the ES barrier during copper deposition. A similar approach could be attempted for ultrathin silver layers.

### 4.2. Sculptured thin films

The term *sculptured thin films* (STF) has been introduced in the 1990s [29]; it refers to nano-engineered materials with columnar morphology tailored to achieve certain properties. Fabrication of such films involves using the atom or ion flux incident on the substrates at very shallow angles and sometimes rotation of the substrate. STF have been used successfully as optical filters [30,31]. Up to now, fabrication of STF has been limited to coatings on small areas. When rotation is not required (i.e., non-chiral STF), the technology could be made compatible with large area deposition processes by using multiple sources "irradiating" the growing structure under shallow angles in a sequential manner. Chevron microstructures represent one type of STF. For example, Fig.3 shows a chevron copper multilayer.
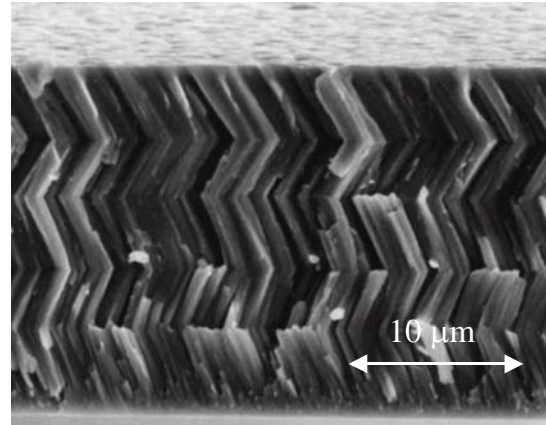


10 μm

Fig.3 Cross section of a chevron multilayer of copper obtained by oblique angle sputter deposition.

### Outlook

Engineering of materials (i.e. design and fabrication) at the nanometer range has many applications including spectrally selective absorption, reflection, and redirection of light. Design relies increasingly on materials computation and characterization, while fabrication is increasingly based on plasma and other processes with precise species and energy control, which in turn require deep understanding and increased use of in-situ process diagnostics [32]. 3-D nano-engineering is limited to small area (although high value) products unless some form of self-assembly is implemented. However, 2-D nano-engineering is fully compatible with large area coatings. In any case, self-organization is most likely the only economical form of large area nanostructured coating. For example, self-organization of island growth can be found in films subject to unequal in-plan biaxial strain [33] and films with strain-induced surface diffusion [34]. By understanding and utilizing the structure-properties-process feedback loop we can expect many novel structures and applications.

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