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Solar Control and Low-Emittance Coatings for Windows
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LBNL Windows and Daylighting Group

Materials, Processes, and Issues in Low-Emissivity and Solar Control Coatings

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Abstract

Research at DOE and other laboratories can help addressing the durability, performance, and cost issues associated with the energy-saving coatings on glass used in windows of residential and commercial buildings. A brief review is presented on the status of energy-savings coatings, including material systems and processes to manufacture them. Issues such as durability, enhanced performance, dynamic coatings, and multifunctional coatings are considered. Industry and the Department of Energy have overlapping areas of interest, and therefore laboratories should and can have a role in energy-savings research and development of industrial relevance. The report includes specific recent results obtained at Berkeley Lab. It is argued that the properties of ultrathin silver films are determined both by the kinetics of the deposition process and the post-deposition thermodynamics of the material system.

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Introduction

Coatings on glass that highly transparent in the visible and reflecting in the infrared are employed for architectural glass and automotive windows for the purpose of energy savings. These low-emittance (low-E) coatings have low emittance and effectively reduce the thermal conductance (U-factor) of a window by suppressing radiative heat transfer. The first low-emittance coatings had a high transmittance across the solar spectrum for maximum solar heat gain. Later products had a high reflectance in the solar infrared to minimize solar heat gain while maintaining high admission of daylight. These products were made of similar materials but with a more complex layer design.

Low-emittance coatings on glass have been developed since the first oil crisis in the 1970s[1] and are now produced in large quantities worldwide[2,3]. The technology is relatively mature. The capacity for architectural and automotive glass coating is about 120 million m^2 annually[4]. Improved energy performance is possible, however costs may be increased. Further penetration into the market depends not only on improved energy performance but also on

- improved silver durability, allowing longer time to elapse between glass coating and IGU (insulated glass unit) manufacturing,
- lower cost to the end user,
- combination with attractive functions such as "self-cleaning" coating and visually adjustable transmission
- specific requirements set by national and regional building codes
- the cost of energy.

While research at DOE laboratories can help addressing the durability, performance, and cost issues, major efforts are underway at industry laboratories. This document is intended to briefly review the status of energy-savings coatings, including material systems and processes to manufacture them, possibilities to further improve energy performance of windows through coatings, identify issues and possibility options to overcome barriers, outline trends and the role DOE laboratories can have. The report includes specific recent results obtained at Berkeley Lab and reviews next steps to be taken.

Industry and Commercial Products

The glass coatings industry has invested millions of dollars to develop a wide range of low-E and solar control products. These products are relatively mature in terms of energy performance and production technology. Two groups of technologies and products can be distinguished:

1. Semiconductor-based coatings, made by CVD (chemical vapor deposition), and
2. Metal (preferably silver) based multilayer stacks, manufactured by PVD (physical vapor deposition), usually magnetron sputtering.

Semiconductor-based coatings often include heavily doped oxides of Cd, Zn, In, and Sn. ITO (indium tin oxide) is preferred when highest conductivity is required, usually in application other than windows, e.g. touch panels at ATMs. Fluorine-doped tin oxide coatings are produced for window glass in large amounts. Semiconductor-based low-E coatings such as SnO_2:F are hard, thermally stable, and corrosion resistant. They can therefore be used for the external of a window (surface no.1), or they can be used on tempered safety glass. However, the sheet resistance is high unless the coating is thick.

Advanced silver-based low-E products contain more than one silver layer, leading to improved reflectivity in the infrared but slightly reduces transmittance in the visible. Figure 1 shows examples of low-E multilayer stacks.

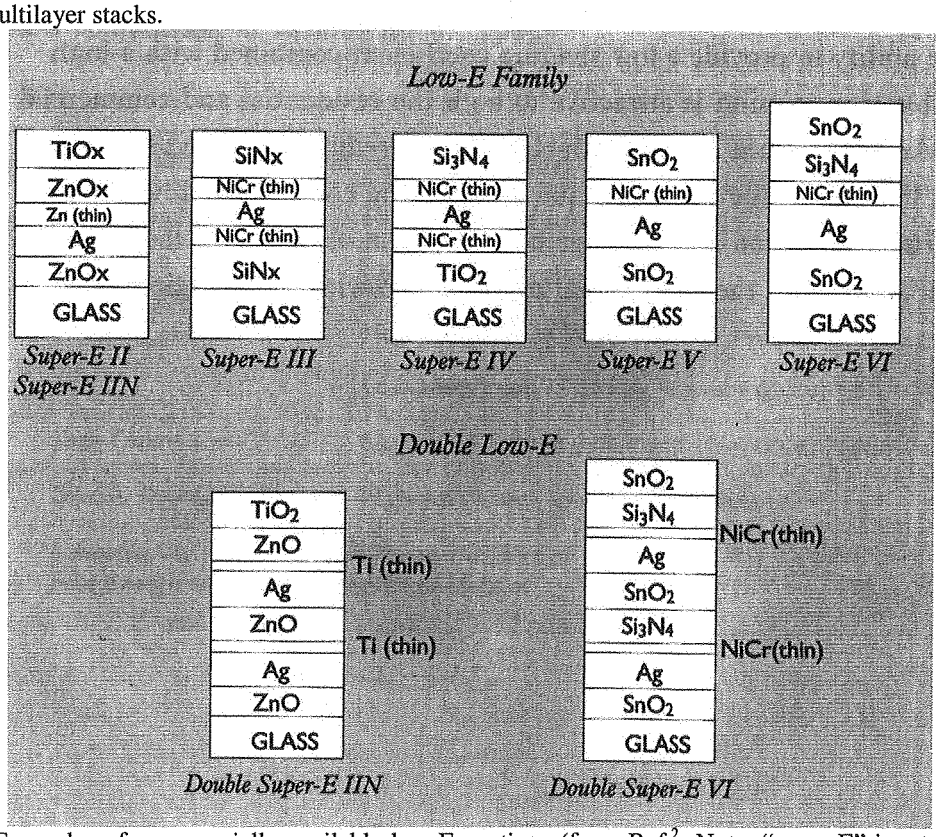

FIG.1: Examples of commercially available low-E coatings (from Ref.[2]; Note: "super-E" is a trademark, used here by permission of VON ARDENNE Coating Technology, Inc.).

Examples of these products can be found on web pages of the manufacturers, for example, but not limited to:

- Guardian Industries (http://www.guardian.com/)
- AFG Industries (http://www.afgglass.com/)
- Visteon (http://www.visteon.com/floatglass/)
- PPG Industries (http://www.ppg.com/)
- Cardinal Glass Industries (http://www.cardinalcorp.com/)

- Pilkington (http://www.pilkington.com/ and http://www.low-eglass.com/)
- Interpane (http://www.interpane.com/main/ and http://www.interpane.net)

A patent search revealed that the area of glass and web coating is actively pursued, both in view of materials and processes. For low-E coatings and coatings processes alone, about 50 patents have been issued over the least years. Quite often, patents describe systems that are discussed in the literature only months or years after patent disclosure, and therefore patents represent an important source of information, which is not always appreciated in the scientific and technical literature.

Materials

As mentioned above, CVD methods are generally related to transparent conducting oxides (TCO), whereas PVD methods include one or more ultrathin metal films in combination with anti-reflection multilayer coatings.

Other approaches can be materials that are intrinsically spectrally selective, such as certain oxides, nitrides, and borides.

In the following, the focus is on PVD-related materials mainly because current resources at Berkeley Lab are geared towards this technology, but also because the highest performing coatings are made this way. Among PVD (sputtered) coatings, the overwhelming majority is silver based because silver has better optical and electrical properties than other metals.

Materials issues of silver-based multilayers concern the following questions:

- What can be done to enhance corrosion resistance, allowing IG manufacturers to store coated glass longer before it is used in IGU fabrication?
- How can the emissivity lowered, transmittance increased, and spectral selectivity improved?

All silver-based products have potential problems with durability partially due to mechanical wear (scratch resistance) but mainly associated with corrosion[5]. Sealing them into insulated glass (IG) units eliminates most of these problems. The coatings are protected from scratching after installation in double pane configuration, and corrosion is practically brought to a hold in well-sealed units. Degradation occurs when the coated glass substrates are shipped, stored, handled, and cut before final IG assembly. Therefore, coated glass products are generally shipped in plastic films with desiccants. The more complex solar control low-E varieties have greater problems with durability. The latest temperable products are even more sensitive, and the biggest durability issues are observed with glue-on retrofit sheets.

Atmospheric silver corrosion occurs in the presence of moisture. If silver is exposed to the atmosphere at room temperature, several monolayers of water vapor will adsorb on the surface[6]. The principal constituent of corrosion layers on silver is acanthite (Ag_2S). The formation of silver sulfide is related to the presence of reduced sulfur. Oxidized sulfur is readily supplied by gaseous SO_2 and by sulfate in airborne particulates. Oxidation to sulfate in solution is readily accomplished by reaction with dissolved hydrogen peroxide or dissolved ozone[6].

In low-E coatings, silver is sandwiched between dielectric layers so direct exposure to the atmosphere is prevented with the exceptions of edge exposure and exposure through pinholes and cracks. Therefore, coatings porosity, expansion and contraction by heat treatment, and edge sealing are important factors for the corrosion resistance of low-E coatings.

Although corrosion by sulfur is the main mechanism, corrosion tests are often performed using chlorine in form of HCl. Pinholes and defects in the coatings can be made visible through corrosion pits (Fig. 2).

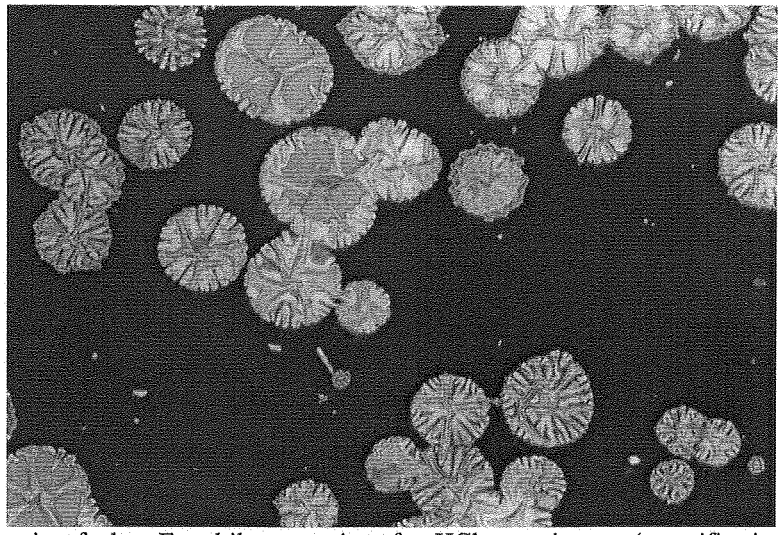

FIG. 2: Corrosion pits of a low-E multilayer coating after HCl corrosion test (magnification 400x; from Ref.[7]).

Several approaches are being investigated to improve silver layers in terms of durability and performance:

- Selection and perfection of suitable underlayers that are smooth and with preferable texture of matching lattice constants (like crystalline ZnO),
- Selection and perfection of encapsulating under and over layers (like NiCr),
- Identification of corrosion-resistant silver alloys that do not compromise silver conductivity and low emissivity in excessive ways
- perfection of deposition processes leading to smoother and denser films (see next section).

Blocking layers are layers that enclose or "sandwich" silver, facilitating preferred texture growth, protecting it from corrosion, and make use of silver-based multilayers on bendable substrate possible. From the recent literature it is known that blocking layers such as NiCr can improve and performance and durability of silver films.

Little is known about the science of materials selection, structure, growth process, and performance of these layers. For example, our preliminary experimental data (section below) show that ultrathin silver layers are not stable but thermodynamically driven to states of lower energy. Therefore, the properties of silver films is determined both by kinetics of the deposition process and the post-deposition thermodynamics of the material system under consideration.

While the above mentioned changes are not intentional, or not intentionally used, modern development points to dynamic coatings, i.e. coatings that change their spectral characteristic as needed or desired. Emphasis is on changes in specific spectral regions, see Table 1, not on changes in all regions.

spectral region	controlled parameter
visible	comfort, glare, privacy
near infrared	solar heat gain
medium infrared	heat loss at room temperature

Table 1: Parameters of relevance in spectrally selective coating.

Examples of dynamic or switchable glazings include electrochromic, gasochromic, and thermochromic materials, which are characterized by phase transition, e.g. by injection of hydrogen or lithium. Funding and research for these coatings are separate and therefore here not discussed further.

Processes

Low-E and solar control coatings can be made by CVD on hot float glass, directly at the float line, or by PVD in large-area coating machines that can be located remotely from the float glass production. The different technologies are associated with different material systems showing low-E properties. In general, processes have important implications on the quality of the product, and therefore careful selection, motioning, control, and adjustment of process parameters is critical for success. Improvements of processes can lead to better product performance (e.g. spectral selectivity) and better economics (reduced use of costly materials, higher yield, etc.)

Focussing on PVD methods, a Varity of plasma-assisted technology was introduced in recent years. Our LBNL-developed low-energy linear gas plasma source (FIG. 3) has contributed to this development.

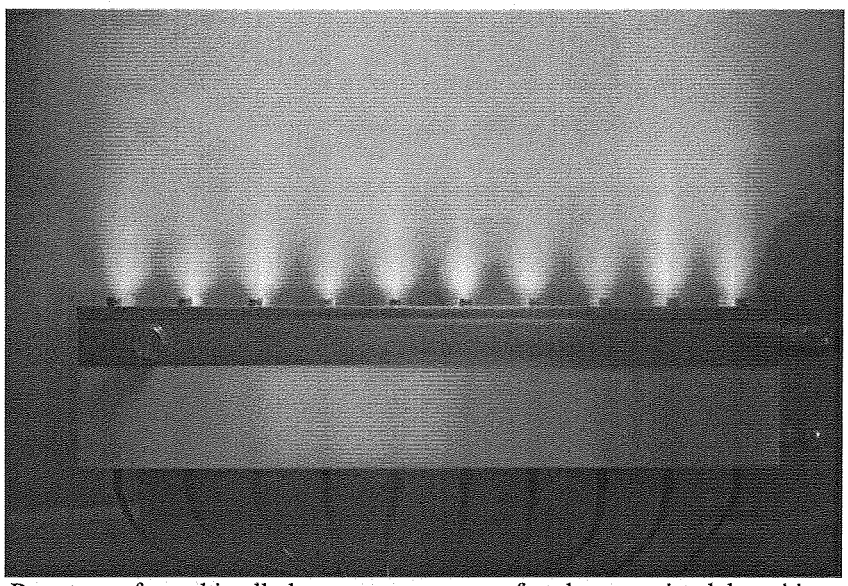

FIG 3: LBNL-Prototype of a multi-cell plasma oxygen source for plasma-assisted deposition of oxide films (from[8]).

Plasma-assistance of deposition processes has the following advantages:

- better control of stoichiometry of compound films, e.g. more complete oxidation of oxide films
- higher deposition rates
- controlled influence on establishment of film texture (i.e. orientation of crystalline grains)
- potentially lower substrate temperatures (still an area of research)
- scalability to large areas possible at reasonable cost

The glass and web coatings industry has started implementing plasma and ion beam assisted technologies. Linear plasma and ion beam sources have become commercially available, although some manufacturers prefer to develop and deploy their own proprietary sources and associated process "precipices." The very wide range of parameters leaves an open field to develop new or improved processes. However, one has to realize that possible improvements in terms of spectral selectivity and associated energy savings are limited due to the maturity of the technologies that have been developed over the last 25 years. Improved plasma processes may help resolving the silver durability issues, improving quality of the product, and improving yield, thereby lowering overall costs, which in turn can boost market penetration.

Recent Work at LBNL

Recent experimental work at LBNL has focused on using exiting filtered arc equipment to explore the influence of ion energy on the growth of ultrathin silver films. The idea is that due to the ion energy,

films may not grow in large islands before forming a continuous film but rather islands are flat and form a continuous film at smaller nominal thickness than in the usual sputtering process. The methodology and results have been reported in a manuscript (LBNL-51307); the essence of this work is reproduced here.

The experimental setup is shown in Fig. 3. A miniature pulsed cathodic arc plasma source[9] with a silver cathode was operated with a ten-stage pulse-forming network.[10] The arc current pulse had a rectangular shape with 1.2 kA amplitude and 620 μs pulse width, with a pulse repetition frequency of 1.6 pulses per second. The plasma source injected streaming silver plasma into a 90° magnetic macroparticle filter[11]. This filter was a curved, open solenoid used to remove microscopic debris ("macroparticles") produced at cathode spots. Neutral silver vapor, if present in the flow, is also removed by the filter, and thus fully ionized silver plasma arrived at the substrates which were located 200 mm from the filter exit. The silver plasma streaming velocity was 11,100 m/s, corresponding to an average kinetic energy of 69 eV, and the mean ion charge state was 2.1 (Ref.[12]). The chamber was cryogenically pumped to a base pressure of about 10^{-4} Pa; no process gas was needed or used.

FIG. 3 Experimental setup for filtered cathodic vacuum (FCVA) arc deposition of thin metal films.

Uncoated glass standard microscope slides, magnetron-sputtered zinc-oxide-coated glass, and titanium-oxide-coated glass were used as substrates. The samples were mounted on a water-cooled substrate holder. The substrate temperature was generally near room temperature although the surface is subject to heating by the deposition process. It is known[13] that the TiO_2 layer is amorphous while the ZnO layer is polycrystalline with {0001} orientation.

Coalescence of silver islands can be detected by measuring the onset of electronic conduction. The film resistance was measured *in-situ* during deposition. For that purpose, two silver contact pads, approximately 1 μm thick, were deposited on the 25 mm wide samples prior to the experiments. The contact pads were 25 mm apart and thus an area of 25 mm x 25 mm was defined. The resistance between the contact pads was measured using a Keithley 617 micro-ohmmeter, directly giving the sheet resistance in Ohms per square.

The deposition rate was calibrated ex-situ by measuring step heights of a thick film (100 nm) using a Dektak profilometer. The nominal thickness of ultrathin films can easily be determined by counting arc pulses under the assumption that the deposited film thickness is directly proportional to the number of arc pulses. This assumption is generally true but an unknown error may occur at the beginning of the deposition process when the oxide is not yet covered with silver. Unfortunately, this is exactly the regime we are interested in. Therefore, nominal thickness should be understood with this shortcoming in mind. The nominal deposition rate was determined to be 0.023 nm/pulse, corresponding to about 1/10 of a monolayer per pulse, an instantaneous rate of 37 nm/s and an average rate of 0.037 nm/s.

For comparison, ultrathin silver films have also been deposited in the same process chamber by DC-magnetron sputtering. The same kinds of substrates were placed 100 mm in front of a 3" sputter gun with a silver target. The argon pressure during sputtering was 66 mPa. The sputter power was 40 W with a target potential of –390 V, leading to a deposition rate of 0.75 nm/s.

The essential results are compiled in Fig. 4. The shape of the sheet resistance curves as a function of nominal thickness indicate three regions: (i) the region of individually dispersed clusters and islands, (ii) a transition region where short link conduction starts, and (iii) a region where a continuous film is formed, gradually approaching bulk resistivity when the film thickness much exceeds the electron mean free path (Drude model). The energetics of the deposition process and the substrate material and temperature are known to affect the transition region and formation of a continuous film. This is illustrated by the difference between the curves for cathodic arc and magnetron deposited silver on glass and ZnO.

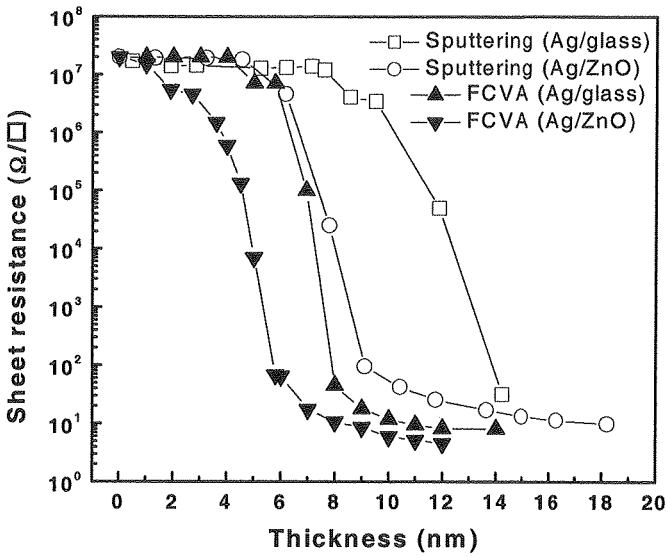

FIG. 4 Sheet resistance of sputtered and filtered arc deposited silver films as a function of incident silver dose, which is expressed as nominal film thickness, measured immediately after completion of deposition.

Focusing initially on filtered arc deposition, it was found that silver on oxides shows a dynamic behavior which is most pronounced in the transition region shown in Fig. 4. At the beginning of the transition, when the sheet resistance was of order 10 MΩ/□, the continuously monitored sheet resistance increased after the cessation of deposition (Fig 5). To rule out electro-migration induced by the current applied in the measuring process, measurements were several times repeated with the ohmmeter either permanently connected or disconnected between measurements. The sheet resistance changed at the same rate regardless of the ohmmeter being connected or not. As successively more silver was deposited on the substrates, the rate of increase in sheet resistance was observed to slow and eventually reverse (Fig. 5). For films with an initial sheet resistance less than a few 10 kΩ/□, the sheet resistance exponentially decreased over time.

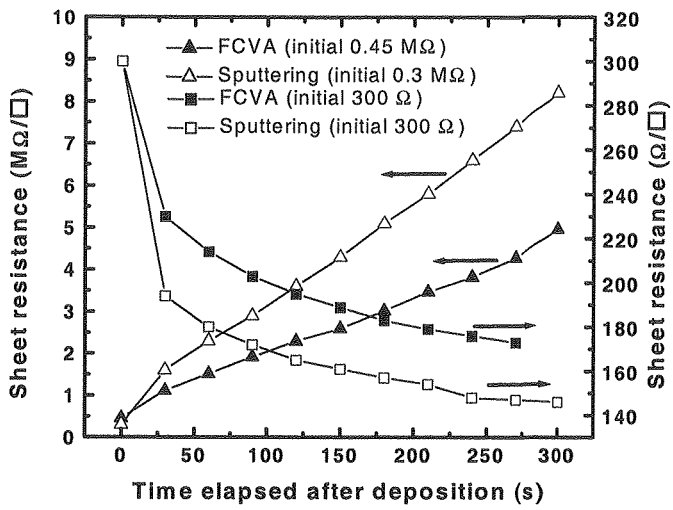

FIG. 5 Sheet resistance of silver films on zinc oxide as a function of time after deposition was stopped.

Since this dynamic behavior of a not-yet-continuous silver film occurs on a timescale much longer than the atomic deposition process, it can be anticipated that sputtered films show a similar behavior. The experiments were repeated with DC magnetron sputtering of silver. The results were very similar as shown in Fig. 5.

The results shown in Figures 4 and 5 are discussed in detail in publication LBNL-51307. It was argued that the energetic differences between filtered cathodic arc deposition and magnetron sputtering lead to distinctly different film properties as shown in Fig. 4. Silver films made by cathodic arc deposition show an earlier onset of island coalescence and formation of short links. This indicates that silver islands in energetic deposition exhibit a reduced aspect ratio when compared to evaporation and sputtering. However, the as-deposited films are thermodynamically unstable, exhibiting "aging" on a timescale of minutes. Whilst films of islands tend to increase their sheet resistance with time, contiguous films show a decrease of the sheet resistance. Both effects can be explained by silver mobility driven to minimize film and interfacial energies. Films made by energetic condensation show lower sheet resistance, implying that low-E and solar control layers made by magnetron sputtering may have a margin for improvement.

Aging indicates that not only the deposition process itself but the sequence and speed of the multilayer coating process is critical. This conclusion is critical for the evaluation of films made in R&D systems: Scaling to larger sizes implies also changes of deposition rates and times elapsed between deposition steps. Ultimately, research results must be reproduced and adapted in production-size coaters, a non-trivial task that should be done with in collaboration with glass manufacturers. The limited validity of small-scale results is also illustrated by the silver deposition on various substrates. While deposition on ZnO-coated glass indicates electronic conduction beyond a certain silver film thickness (Fig. 5), TEM (transmission electron microscope) pictures of the same deposition but on thin Si_3N_4 membranes shows that Ag is in islands (Fig. 6). Therefore, one has to be very cautious when generalizing results found under a certain set of parameters (substrate material, thickness, temperature, deposition rate, etc).

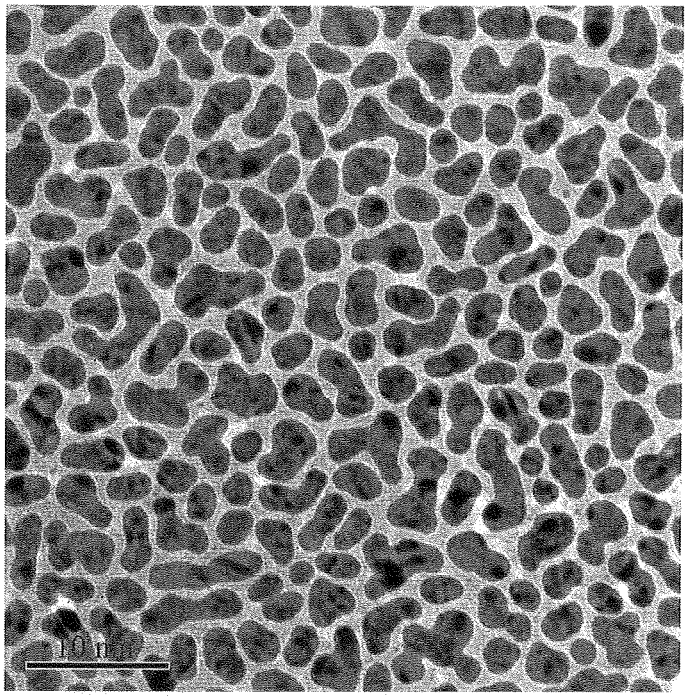

FIG. 6 *Islands* of silver grown on a Si_3N_4 membrane using filtered cathodic plasma deposition; films of the same nominal thickness grown on ZnO-coated glass using the same technique indicate electronic conduction of a *continuous* film (Picture taken at the National Center for Electron Microscopy, Berkeley).

Summarizing this section, it has been shown that the kinetics of the deposition process can be controlled, or at least affected, by the energy of film-forming particles. However, if the resulting film is thermodynamically not in a stable low-energy state, thermodynamic forces can drive changes of the film on a much longer time scale than the duration of the deposition process. The implication is that R&D results obtained under R&D conditions in small R&D chambers can only serve to clarify materials processes but they cannot be directly transferred to production-size and production-rate processes.

Outlook

In this section, ideas and plans are outlined which in part constitute the current Statement of Work and which in part point to possible new directions of research.

1. Improving the performance and durability of silver-based low-E coatings by selecting and optimizing suitable "blocking layers"

Blocking layer materials can be pre-selected based on thermodynamic, optical, electrical, and chemical properties (hence avoiding a trial and error approach), and pre-selected materials can be used in a deposition chamber dedicated to the efficient synthesis of a large number of samples in a combinatorial-synthesis-like manner. Patents have been issued on the use of certain materials, such as NiCr, which is also shown in Fig. 1. So far, suitable materials have been identified by trial and error; research should be used to systematically characterize interfaces using a range of methods, allowing us to understand the physical and chemical principles of silver interfacing with other material. Characterization should be complimented by computer simulation of optical properties. The difficulty is to understand the interrelation between process kinetics, post-process thermodynamics, and intrinsic properties of material, as well as material interaction (solubility, diffusivity, optical constants, practicality, and economics). The findings should be transferred to in-line coating machines that much larger and closer to real production coaters, emulating relevant rates and sequences of deposition.

2. Development of improved or alternative high-rate, low-cost processes for advanced coatings

Apart from CVD coatings performed in in-line coaters on the still-hot float glass, sputtering is the method of choice for glass coating. Both CVD and sputtered films are not fully dense and characterized by columnar structure. Material properties can be enhanced by producing dense films, for example, the protective barrier effect would be improved if voids were eliminated.

Higher rates can be achieved by "activating" the reactive gas supply, which is usually done through plasma generation. Combining sputter deposition with plasma generation was shown to be beneficial for deposition rate and quality of the coating. Additionally, linear plasma sources can be used to effectively clean glass substrates, surface-activate plastic webs, and assist in the deposition of protective layers. The implementation of plasma processes by coating companies shows that they realize that the quality of coatings can be improved and the overall costs can be reduced, helping not only to accomplish broader introduction of advanced glazing but also improve their competitive position.

"Energetic Condensation" is a promising technique for synthesis of dense films. In essence, condensing, film-forming species need to have hyperthermal energies, e.g. typically in the range 10-100 eV. The emerging technique of reactive arc deposition has the potential to revolutionize the industry if a number of technical issues can be resolved. Alternatively, metal sources can be integrated with gas plasma sources. If the latter operate with reactive gases (such as oxygen and nitrogen), compound films (such as oxides and nitrides) can be deposited, while the operation with inert gases could serve for low-energy ion assisted growth. Research of this kind may also address the issue of substrate temperature. Lower temperature would reduce production costs, ease manufacturing difficulties, and save energy in the production process, assuming that the energy consumption of the plasma source is less than the energy needed to bring the substrate material to the high substrate temperature required for some coating processes.

3. Development of alternative materials for improved coatings

With advanced processes available, new materials can be developed, and existing materials can be modified and enhanced. Materials have to fulfill several functions at once, and thus it is highly desirable to tune or tailor materials properties. For example, it is desirable to make adhesion layers and overcoat layers with desirable refractive index, interface energy, and hardness.

By controlling film composition, density, and texture, one can adjust material properties. It is conceivable to design materials that have optimized refractive index, surface energy, and mechanical properties. An example is TiO_2 whose refractive index can be shifted in a certain range as determined by coatings conditions. Co-deposition of composite (like ternary) oxides is a field not sufficiently explored or utilized. Close relation between synthesis and characterization, and practical application for energy-savings applications needs to be established.

Of specific interest are new or improved transparent and conducting materials such as heavily doped zinc oxide, which potentially could replace ITO in same applications.

4. Study of the limited equivalence of plasma and temperature

Temperature is a crucial parameter for film growth. "Temperature" in conventional deposition means the substrate temperature, though the situation is more complicated in energetic condensation. Ions deliver both kinetic and potential energy to the substrate[14]. For example, on average, a cathodic arc silver ion delivers 105 eV total energy to the substrate[12], which greatly exceeds the lattice and surface binding energies. While the kinetic energy determines the subplantation range, potential energy contributes to local heating.[14] The total energy is released in a nanoscale thermal spike, when important processes such as diffusion, defect annealing and surface atom migration can occur rapidly.

As shown by the above example, plasma processes imply heating of the growing film without having the substrate at high temperature. However, plasma "heating" involves kinetic processes far from thermodynamic equilibrium, while high substrate temperature drives thermodynamically preferred processes. The interrelation of kinetic and thermodynamic process control is not fully understood or utilized, and has the potential for important contribution to science and practical applications.

5. Exploration of unconventional materials and concepts

With the rapidly developing field of nanoscience and high-resolution characterization and imaging, new opportunities may arise. For example, nanocomposite materials can show interesting optical properties like low emissivity and high absorbance; these properties are not necessarily desired for

windows but may be utilized in the larger framework of facades and building envelopes. Of particular interest are technologies for "dynamic" (switchable) products. For example, highly desirable is system that could tune the wavelength of transition between transmission and reflection of radiation in the infrared part of the spectrum, e.g., low-E coating with tunable solar heat gain. Coating technologies developed for window glass coating may be used for other products, such as large area photovoltaic devices, and technologies developed for other products may impact the design and making of energy-efficient windows. A DOE-sponsored program can benefit from such synergetic effects.

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