MICROSTRUCTURE AND OPTICAL PROPERTIES: SEVERAL INTERESTING APPLICATIONS

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I. INTRODUCTION

Materials with tailor-made radiative properties are useful for harnessing the Sun's energy, for creating a new energy-efficient architecture, etc. The materials optimization must be done with consideration of the radiation that prevails naturally in our surroundings. This paper discusses this "natural" radiation, and uses its characteristic properties to devise coatings for various types energy-efficient applications. Emphasis is put on large-area chromogenics, which enables "smart windows" to be realized. A particularly interesting alternative uses electrochromic thin films to regulate the throughput of radiant energy so that a desirable indoor temperature and a desirable level of illumination can be maintained.

Section II introduces spectra for thermal and solar radiation, for atmospheric absorptance, and for visible and photosynthesis-active light. This information leads naturally to a series of materials — often used as coatings — for some energy efficient applications. We then focus on electrochromics, and Section III reports on a basic devise design, a case study for the electrochromism in tungsten oxide, and some practical approaches to smart windows. Section IV gives a few final remarks. This paper is a revised version and update of a recent article [1].

II. AMBIENT RADIATION AND MATERIALS OPTIONS

A. Ambient Radiative Properties

The basic principles of materials for energy efficiency and solar energy conversion can be grasped only if one has a clear idea of the radiation that prevails in our natural surroundings [2]. This radiation is introduced in Fig. 1, where the different spectra are drawn with a common logarithmic wavelength scale. We start with the ideal blackbody, whose emitted spectrum is uniquely defined if the absolute temperature is known. Figure 1(a) depicts blackbody spectra for four temperatures. The vertical scale denotes power per unit area and wavelength increment. The spectra are confined to the $2 < \lambda < 100$ μm wavelength range. At room temperature the peak lies at about 10 μm. Thermal radiation from a real

material is obtained by multiplying the blackbody spectrum by a wavelength-dependent factor — the emittance — which is less than unity.

Figure 1 (b) reproduces a solar spectrum for radiation outside the earth's atmosphere. The curve is defined by the Sun's surface temperature (~ 6000°C). The solar spectrum is limited to the $0.25 < \lambda < 3$ μm interval, so that there is almost no overlap with the spectra for thermal radiation. Hence one can have materials whose properties are entirely different with regard to thermal and solar radiation. The integrated area under the curve gives the solar constant (1353 ± 21 Wm^{-2}); this is the largest possible power density on a surface oriented perpendicular to the sun in the absence of atmospheric extinction.
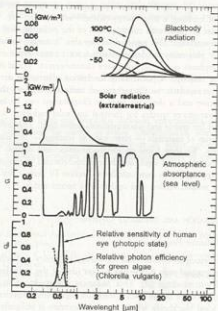

Fig. 1 - Spectra for (a) blackbody radiation pertaining to four temperatures, (b) solar radiation outside the earth's atmosphere, (c) typical absorptance across the full atmospheric envelope, (d) relative sensitivity of the human eye and relative photon efficiency of green algae. (From Ref. 2).

We are concerned with systems at ground level, and it is of obvious interest to consider to what extent atmospheric absorption influences solar irradiation and thermal emission. Figure 1(c) illustrates a typical absorption spectrum vertically across the full atmospheric envelope during clear weather conditions. The spectrum is complicated with bands of high absorption — caused mainly by water vapour, carbon dioxide, and ozone — and intervening bands of high transparency. The majority of the solar radiation can be transmitted to ground level.

Thermal radiation from a surface exposed to the clear sky is strongly absorbed except in the $8 < \lambda < 13 \mu m$ range, where the transmittance can be large provided that the humidity is moderately low. The thermal radiation can be large in the $8 < \lambda < 13 \mu m$ interval, and hence a nonnegligible part of the emitted energy can go straight through the atmosphere. This phenomenon constitutes the basis for radiative cooling.

Figure 1(d) illustrates two biophysical constraints of interest for glazings. The solid curve shows the relative spectral sensitivity of the human eye in its light-adapted (photopic) state. The bell-shaped curve extends across the $0.4 < \lambda < 0.7 \mu m$ interval and has its peak at 0.555 μm. Clearly a large part of the solar energy comes as infrared radiation. Photosynthesis in plants operates with wavelengths in approximately the same range as those for the human eye, which is of relevance for greenhouses.

B. Survey of Coatings for Energy Emcient Glazings

Coatings can be used on glazings for obtaining several different goals. Table I summarizes these goals, gives the principle solutions, and lists the different types of materials used in the coatings [3]. In a warm climate, the glazings normally let in too much energy, which must be balanced by air conditioning. The situation can be alleviated if the windows have coatings that are transparent primarily for visible light, i.e. at $0.4 < \lambda < 0.7 \mu m$, whereas they are reflecting for near-infrared solar radiation at $0.7 < \lambda < 3 \mu m$. A thin metal (Me) film can combine a transmittance of ~50% in the visible range with a high infrared reflectance. However such a film is too absorbing for many applications, and instead the metal film could be put between two dielectric (D) layers which, in effect, antireflect the metal. A D/Me/D coating with Me = Ag can have ~ 80% visible transmittance.

Another way to diminish the solar inflow is to exploit angular-selective window coatings [4, 5]. The underlying idea is that windows are devices for creating visual contact with the outside world along an approximately horizontal line-of-sight, whereas solar radiation normally enters from a point much higher up on the vault of heaven. It follows that one can obtain energy efficiency by having coatings with high transmittance horizontally and a much lower

Table I — *General properties of coatings for energy-efficient glazings.*

Goal	Principal solution	Coating material *
Diminished solar heating	Reflectance at $0.7 < \lambda < 3 \mu m$	Me or D/Me/D
	Angular dependent transmittance	D/Me/D/Me/D Oblique columnar metal
Thermal insulation	Reflectance at $3 < \lambda < 50 \mu m$	D/Me/D, SnO_2:F, In_2O_3:Sn, ZnO:Al...
Dynamic radiation control	Absorptance or reflectance in electrochromic material	Li_xWO_3, $Ni_{1-x}H_xO_y$,... in multilayer design with transparent ion conductor
	Reflectance at $0.7 < \lambda < 3 \mu m$ in thermochromic material	VO_2-based
Higher transmittance	Antireflectance at $\lambda = 0.55 \mu m$	AlO_xF_y,...

* Me is Ag, Cu, Au (or Al); D is Bi_2O_3, In_2O_3, SnO_2, TiO_2, ZnO or ZnS.

transmittance at other angles. A properly tailored D/Me/D/Me/D coating can be useful for ordinary vertical windows. Angular selectivity can be created also for sloping glazings; in this case the coatings can be comprised of inclined columns produced by oblique angle vacuum deposition. For the latter case, one has a higher transmittance along the columns than across them, as one expects from effective medium theory.

In a cold climate, one normally wants to have glazings that combine a high solar transmittance at $0.3 < \lambda < 3 \mu m$ with a high reflectance (i.e., a low emittance) for thermal radiation at $3 < \lambda < 50 \mu m$. D/Me/D coatings can be optimized for these wavelength intervals, but it may be more cost-effective to invoke films of certain heavily doped wide-bandgap oxide semiconductors such as In_2O_3:Sn, SnO_2:F, SnO_2:Sb and ZnO:Al. When the doping level is high enough, the semiconductors become strongly n-doped and can be reflecting at wavelengths longer than a plasma wavelength that can lie between 1 and 3 μm depending on the doping level and the degree of crystallinity [6, 7].

A dynamic control of the optical properties is possible in smart windows with chromogenic coatings. The presently most viable alternatives are electrochromic films in multilayer devices, as discussed in the following section, and thermochromic films. Among the thermochromic films, the most important ones are based on VO_2. This material undergoes a monoclinic → tetragonal transforma-

tion from a semiconducting and rather transparent state to a metallic and less transparent state when a temperature of − 68°C is exceeded. This phase change temperature can be diminished to room temperature by alloying with tungsten [8] and the transmittance can be boosted by fluorine incorporation [9].

III. Electrochromics and Smart Windows

A. Background

Electrochromic devices are able to change their optical properties in a reversible and persistent manner under the action of a voltage pulse. The optical modulation is related to the amount of mobile ions in an electrochromic material, which here is taken to be a metal oxide. The devices comprise several layers backed by a substrate (normally a glass plate) or layers positioned in between two substrates in a laminate configuration [10, 11]. The substrate has a transparent conducting film and a film of the electrochromic oxide [11]. Then follow a fast ion conductor or electrolyte, a layer serving as ion storage — which can be another electrochromic material — and a second (transparent) conductor. When a voltage is applied between the (transparent) conductors, ions are inserted into or extracted from the electrochromic film, whose optical properties thereby are changed. The design is outlined in Fig. 2. The insertion/extraction process can be represented, high schematically, by

$$MeO_y + xI^+ + xe^- \leftrightarrow I_xMeO_y, \qquad (1)$$
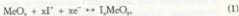
where I^+ is a singly charged small ion such as H^+ or Li^+, e^- an electron, and y depends on the particular type of oxide. For example, y is 3 for defect perovskites and 2 for rutiles.

Electrochromic devices have several important applications that presently spur the scientific and technical development. Foremost among these are smart windows capable of regulating the inflow of radiant energy through glazings so that an optimum indoor climate is maintained at a minimum demand on paid energy.

B. Electrochromism in W Oxide: A Case Study (Ref. 10)

Electrochromism was discovered in W oxide films, and this material remains still today the most promising with regard to practical applications. There are many techniques for making W oxide films. Evaporation, sputtering and a number of chemical and electrochemical methods all are applicable and are able to produce non-stoichiometric WO₃ films with a porosity of up to
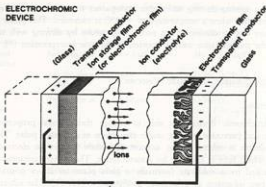
Fig. 2 · Basic design of an electrochromic device, indicating transport of positive ions under the action of an electric field.

50%. Raman scattering and X-ray extinction, in particular, have been used to formulate microstructural models [12] showing that the films are built from clusters of comer-sharing octahedra.

W oxide films have been studied extensively in liquid electrolytes by use of the conventional techniques of electrochemistry. Coulometric titration, chronoamperometry, cyclic voltammetry, impedance spectrometry, beam deflectometry, and microbalance techniques [10] have been applied. The diffusion constants for intercalation/deintercalation of H^+ and Li^+ lie in the ranges 10^{-10} to 2.5×10^{-8} and 1.1×10^{-12} to 5×10^{-9} cm^2/s, respectively.

X-ray photoelectron spectroscopy in the energy range pertinent to $W4f$ electrons shows peaks that allow the amount of W atoms in different valence states to be calculated. For H_xWO_3 with $x = 0.09$ it was possible to represent the spectrum with two sets of peaks assigned to W^{5+} and W^{6+}, and at $x = 0.42$ there was clear evidence also for W^{4+} [13]. Electron paramagnetic resonance is capable of providing additional information on the valence state of the W since W^{5+} ($5d^1$ configuration) gives a signal due to its unpaired spin whereas W^{6+} ($5d^0$ configuration) does not. Experimental data showed unambiguously that a signal assigned to W^{5+} developed upon H^+ intercalation [14].

Figure 3 shows the modulation of the spectral transmittance upon intercalation to the shown charge densities in a H^+-conducting electrolyte [15]. The W-oxide-based film can change reversibly and gradually from a virtually transparent state to a state characterized by a low transmittance of blue light.
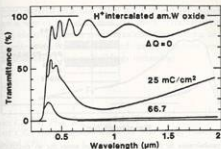
Fig. 3 - Spectral transmittance for an "amorphous" (am.) W oxide film with H⁺ intercalation to the shown charge densities. (From Ref. 15).

The small polaron concept offers a possibility to formulate a quantitative theory for the optical absorption. Small polarons are created when electrons polarize their surroundings so that localization of the wavefunction takes place essentially on one lattice site. A small overlap between wavefunctions corresponding to adjacent sites, as well as strong disorder, are conducive to polaron formation. Theoretically, the small polaron absorption α_{pol} can be expressed by

$$\alpha_{pol}(\omega) \propto \omega^{-1} \exp \left[-\frac{(\hbar\omega - 4U_p)^2}{8U_p\hbar\omega_{ph}} \right], \qquad (2)$$

where U_p is the polaron binding energy and $\hbar\omega_{ph}$ is a typical phonon energy. $U_p = 0.275$ eV and $\hbar\omega_{ph} = 0.098$ eV were able to bring theory and experiment into acceptable agreement [16].

C. *Towards the Electrochromic Smart Window* (Refs. 10, 11, 17)

Practical electrochromic devices have an electrolyte at their center as seen in Fig. 2. Liquid electrolytes, that are commonly used in laboratory studies, are not of interest for the optical window applications. Also many of the standard members of the solid state ionics zoo (β-aluminas, Nasicons, etc.) are not easily used since it is difficult to make thin films of them. Hydrated oxide films are of relevance, and devices with a Ta₂O₅·H₂O film in between layers of cathodic electrochromic W oxide and anodic electrochromic Ni oxide are currently exploited for rear-view mirrors in automobiles. Whereas this approach may be suita-
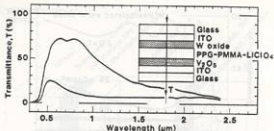
Fig. 4 - Spectral transmittance in coloured and bleached states for an electrochromic device with a Li⁺-conducting electrolyte. The design is sketched in the inset. (From Ref. 20).

ble for small devices, one may question its usefulness in large smart windows to be used for energy-efficient glazings. It appears that polymer electrolytes are more promising for smart windows.

Extensive work has been carried out with proton conducting polymers such as polysulfonic acids. These polymers tend to corrode W oxide films, though, and therefore the interest has shifted more towards Li⁺ conducting polymers. Initial work was reported for devices with polyethylene oxide (PEO) incorporating $LiClO_4$ [18]. These "windows" exhibit temperature dependent electrochromism, but operation at room temperature requires more conducting electrolytes. One interesting possibility is $PEO-LiN(SO_2CF_3)_2$, which was used in some recent studies [19]. Devices with "amorphous" W oxide and ion storage layers of V_2O_5 showed transmittance modulation between ~ 41 and ~ 13% at $\lambda = 0.633$ µm. Device operation at room temperature is possible also with multilayer structures based on W oxide, V_2O_5, and an intervening adhesive electrolyte of poly propylene glycol (PPG) and poly methyl methacrylate (PMMA) [20]. Figure 4 illustrates the latter design and shows spectral transmittance in coloured and bleached states. At $\lambda = 0.633$ µm, for example, the transmittance can be modulated between as much as ~ 72 and ~ 20%. Results are available also with lithiated Ni oxide used as ion storage layer.

IV CONCLUDING REMARKS

A large number of novel materials can be used for solar energy applications and for creating energy efficiency in many different contexts. Some of these materials are now reaching maturation, such as selectively solar-absorbing films

and transparent infrared-reflecting films for architectural glazings. Other materials still have a way to go before they can reach commercialization; smart windows based on electrochromism and thermochromism belong to this class. Large area chromogenics, electrochromism, and smart windows are likely to have important applications in benign buildings technology.

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