Progress Report: Optical Properties of Thermochromic VO_2 Coatings for Windows

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ABSTRACT

The properties of VO_2 thermochromic coatings were investigated for application to building windows. The solar transmittance of VO_2 decreases above a certain temperature, blocking excess solar gain. Films were deposited on glass by reactive magnetron sputtering, but stoichiometric compositions have not yet been achieved. The composition and structure of these films have been determined by Auger spectroscopy and x-ray diffraction. Optical properties were measured by photometric and ellipsometric methods. Using this optical data, composite coatings were designed having improved optical characteristics. The high-temperature metallic state of VO_2 was not found to be suitable as a static low-emissivity coating. When this VO_2 is used as a thermochromic coating, however, its moderately low emissivity would contribute to energy savings. The ratio of solar transmittance between the high-temperature and low-temperature states increases with decreasing average transmittance. Higher values of this ratio might be obtained by proper choice of additional coating layers.

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Introduction

Thermochromic materials have optical properties that change with temperature. A material that transmits solar radiation at low temperatures and reflects solar infrared radiation at high temperatures would make a useful optical switch for building glazings. In this report we describe the properties of one thermochromic material, VO_2, and its potential for use as a window coating.

Photochromic materials, which respond to light as a thermochromic material responds to heat, are also being developed for building applications. The photochromic response, however, is best suited to control glare rather than energy transfer. For example, on a bright cold day, a photochromic window would eliminate desired solar heat gain.

Electrochromic materials, which respond to an applied electrical signal, can be controlled with complete flexibility. A set of heat and light sensors connected to a building management computer could decide the optimum schedule for an electrochromic shutter. In addition, a manual override could close the shutter at any time for privacy. For these reasons electrochromic coatings are the subject of intensive research. The main disadvantage of electrochromic windows compared to thermochromic or photochromic windows is the additional complexity of the window from the viewpoint of manufacturing, assembly, and installation.

Conventional solar-control and low-emissivity coatings have achieved popularity with the industry because the finished product has many of the same dimensional characteristics and fabrication requirements as an uncoated sheet of glass. Thermochromic (and photochromic) coatings retain this advantage. This is especially desirable for residential use because the cost of an expensive control system would be spread over far fewer windows than in a commercial building. Also, a thermochromic coating would be much simpler in structure than an electrochromic coating, thus reducing manufacturing costs.

To evaluate the potential of this particular material as a thermochromic optical shutter, we must find its optical properties. From measured photometric properties the fundamental optical constants can be determined. This information can be used to predict the optical properties of a wide variety of VO_2-based films. First, we consider the potential of VO_2 as a static low-emissivity coating. Then, we investigate the magnitude of the dynamic thermochromic effect.

Methods and Results

Jorgenson [1] surveyed the known thermochromic materials. He concluded that VO_2 best fits the requirements for a window coating because of its appropriate transition temperature and its large change in optical properties. As the temperature rises above the transition temperature, VO_2 changes from a semiconductor to a metal. The discontinuous change in energy band structure results from a change in crystal structure. Semiconducting VO_2 has a monoclinic MoO_2-type structure that contains pairs of more closely spaced V atoms. Metallic VO_2 has a tetragonal rutile structure with evenly spaced V atoms.

Goodenough identified possible mechanisms for this transition and suggested that introducing extra electrons by impurities would reduce the transition temperature [2]. Horlin [3] and Jorgenson [4] produced a reduction in transition temperature by doping with tungsten. A simple empirical relationship was found between the transition temperature and the doping level: $T_t \approx 68 - 2600x$, where T_t is the transition temperature in $^\circ C$ and x is the dopant concentration in $V_{1-x} W_x O_2$.

Although the transition temperature can be set over a wide range by doping during deposition, once set it cannot be changed. The optimum transition temperature for a thermochromic window depends not only on the optical properties of the film, but also on the daily and annual patterns of temperature and sunlight, the type and orientation of the window, the type of building, and even the habits of the occupants. These factors can only be accounted for in a detailed annual energy calculation. Next year we will perform such calculations to determine optimum transition temperatures under a variety of conditions. Meanwhile, it is enough to know that T_t can be varied over the probable range of desired temperatures. First, we must determine the optical properties of VO_2 and if possible improve them by multilayer coating design.

We deposited VO_x films onto glass substrates by rf magnetron sputtering of a V target in an $Ar-O_2$ mixture at 10_{-2} $torr$. The phase composition was investigated using x-ray diffraction. These films confirm the rough phase diagram of Griffiths and Eastwood [5]. Films deposited without substrate heating are uniform, yellow, and amorphous. Polycrystalline VO_x films result for substrate temperatures between 350 and 500 $^\circ C$ and O_2 partial pressures between 0.07 and 0.14. Films 1000A thick, deposited under these conditions, have a translucent gray-yellow appearance. Substrate temperatures above 500 ^{o}C produced very nonuniform films, possibly due to a nonuniform substrate temperature.

Analysis of film composition by Auger electron spectroscopy indicates that we have not yet achieved stoichiometric VO_2. Because of this, the optical quality of these films can probably still be improved. Also, we have not yet made films with doping which could have profoundly different optical properties. Meanwhile we can obtain much useful information from the optical properties of currently available samples. The results that follow have been compared to those of Verleur [6] and Barker [7] with good qualitative agreement, considering that our films are not yet stoichiometric.

The transmission and reflection of each interesting deposited film were measured over a wide spectral range. The solar spectra were recorded by a Perkin-Elmer Lambda-9 spectrophotometer and the thermal infrared spectra by a Mattson Fourier-transform spectrometer. This is enough information to characterize these films for the present application. To design improved coatings, however, the optical constants of the as-deposited material is needed. One method for obtaining these optical constants uses a self-compensating scanning ellipsometer. Although this is our most reliable technique, the ellipsometer covers the visible spectrum only. The optical constants can be determined over the entire spectrum of interest by numerical solution of the complex equations for the measured photometric properties. Using these methods we now have a complete set of values to work with, but the process must be repeated when stoichiometric and doped samples are obtained. The following results are calculated from this fundamental data.

The high temperature metallic phase of VO_2 has optical properties similar to those of a noble metal. For thin semitransparent films (Fig. 1) there is a pronounced transmission maximum in the visible, decreasing rapidly to near zero in the infrared where the reflectivity steadily increases. These are the properties that are generally desirable in a low-emissivity coating. Before considering the thermochromic behavior, we therefore investigated the possibility of using undoped VO_2 conventional low-e coating having static properties.

As usual, there is a trade-off as thickness changes between the two desirable properties of a low-e coating: visible or solar transmission versus infrared reflectivity. We optimized the properties of composite low-e coatings using a conventional 3-layer design, where the middle layer is VO_2 and the outer layers are dielectric (non-absorbing) antireflection layers. In this preliminary study, we treated the dielectric layers by parametrically varying their index of refraction n, which was assumed to be constant over the entire spectrum. The greatest enhancement in visible transmission was achieved for dielectric layers having $n \approx 2.5$. The sensitivity of the results to changes in n, however, was very slight.

Figure 2 shows the optimum value of average visible transmission versus average infrared reflectivity for the 3-layer composite with $n = 2.5$. The transmission values for this curve are significantly higher than for the single-layer VO_2 curve. In absolute terms, however, the 3-layer coating does not have sufficiently high optical selectivity to be considered as a non-switching low-e coating. To demonstrate this, we include a curve for an optimized TiN-based low-e coating, which shows far superior performance to the VO_2 curve. Because TiN has at best average optical selectivity among low-e materials, this eliminates VO_2 from consideration.

Although not able to compete with other materials as a static low-e coating, VO_2 transforms to a semiconducting state at low temperature. In the low temperature state, the solar transmission of VO_2 increases. Fig 3. shows that the most pronounced change occurs in the solar infrared while the visible transmission remains more steady. The infrared reflectivity (not shown) is considerably lower than in the metallic state. At the transmission level of Fig. 3 the infrared reflectivity is about 0.1 and has a maximum of about 0.3 for thick films.

The apparent magnitude of the thermochromic transition is somewhat exaggerated by the scale of Fig. 3, because the energy available in the solar spectrum decreases throughout the solar infrared. This effect can be accounted for by averaging the transmission of the films over the solar spectrum weighted by the spectral irradiance. Figure 4 summarizes the results for films of various thicknesses. The ratio of average solar transmittance for the two states is greatest for films of small absolute visible transmittance (small thickness). For films with visible transmittance over 0.2 the ratio is less than 1.5.

Accomplishments and Future Research

We successfully produced reactively sputtered films of nearly stoichiometric VO_2, and set up the techniques necessary to analyze their composition, structure and optical properties. We obtained a set of optical constants which are of fundamental value for any industry groups interested in applications of this material. We designed composite films with maximized visible transmission. These films were found to have poor optical properties when considered as static low-e coatings. The magnitude of the thermochromic effect was found to be greatest for films of low average transmittance.

In FY87 we intend to modify our deposition process to produce doped films having altered transition temperatures and optical properties. A set of optical constants will be generated for these films. Optimum transition temperatures will be determined by simulations of annual energy performance. Improvements in the solar transmittance ratio might be possible by a judicious choice of matching layers as discussed above in connection with low-e properties.

Acknowledgement

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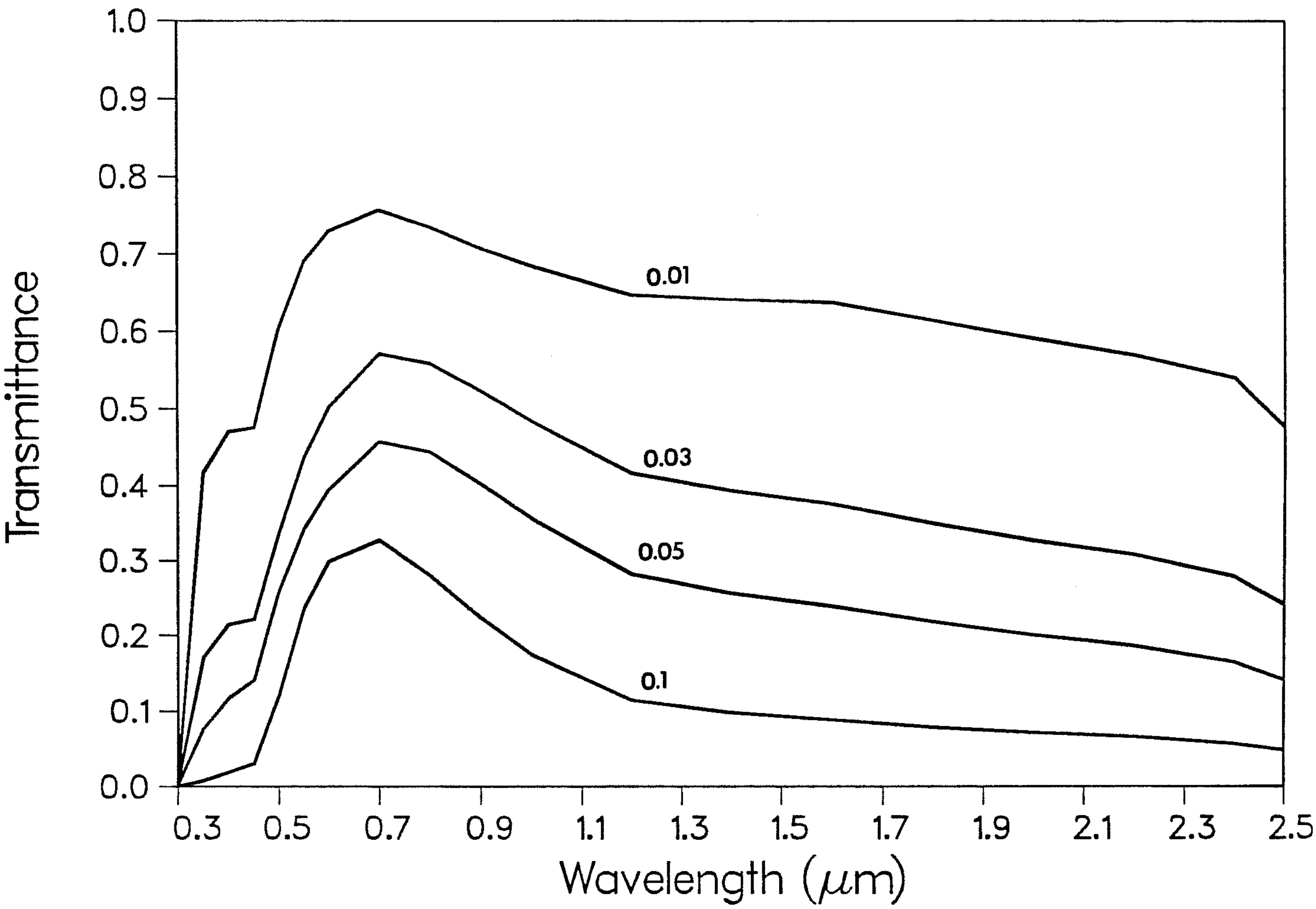

Figure 1. Transmittance over the solar spectrum for VO_2 films of various thickness (0.01, 0.03, 0.05, and 0.1 μm) on glass.

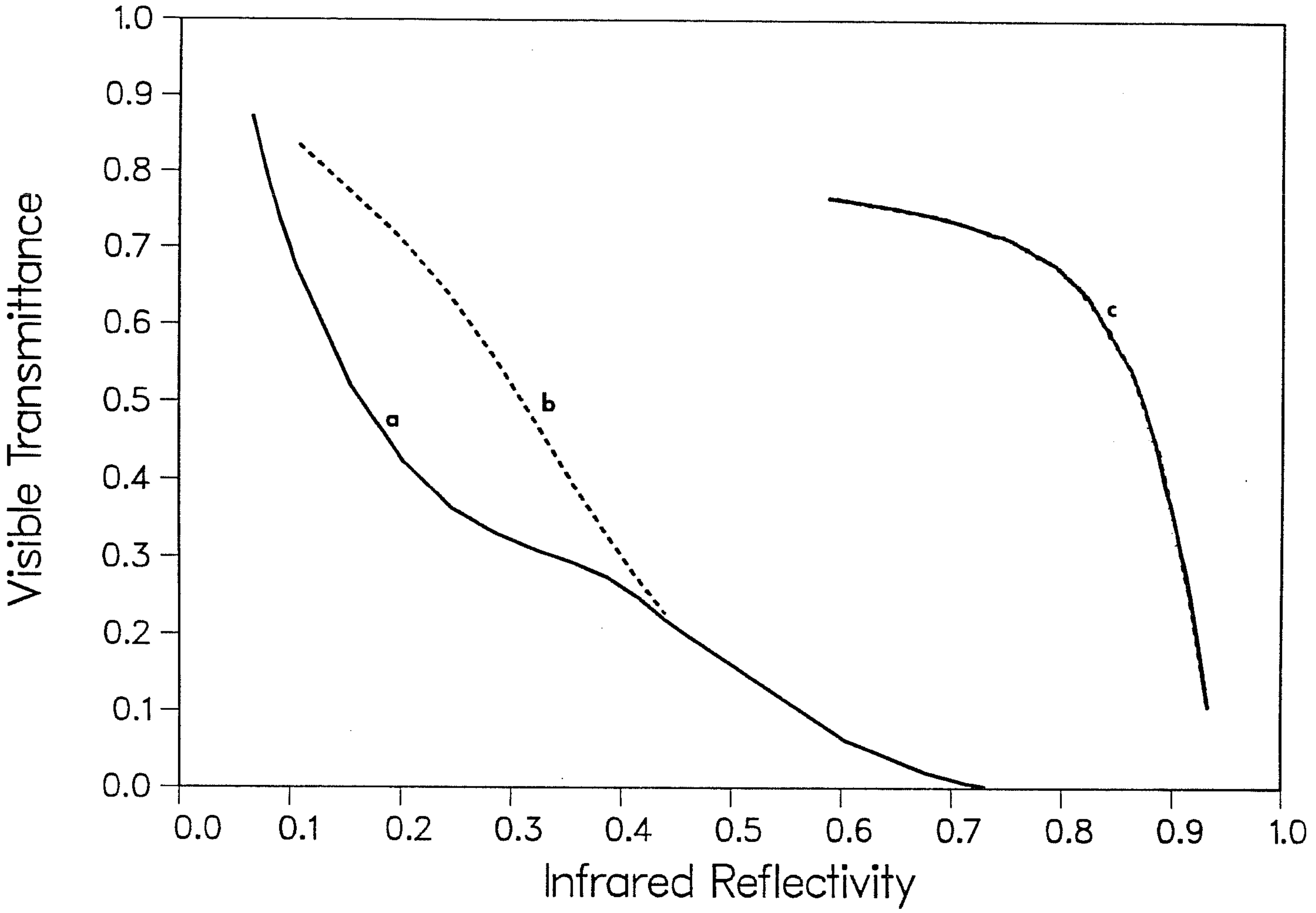

Figure 2. Visible transmittance and infrared reflectivity measure the performance of low-emissivity coatings: (a) single-layer VO_2 coatings (b) optimized triple-layer VO_2-based coatings and (c) optimized triple-layer TiN-based coatings for comparison.

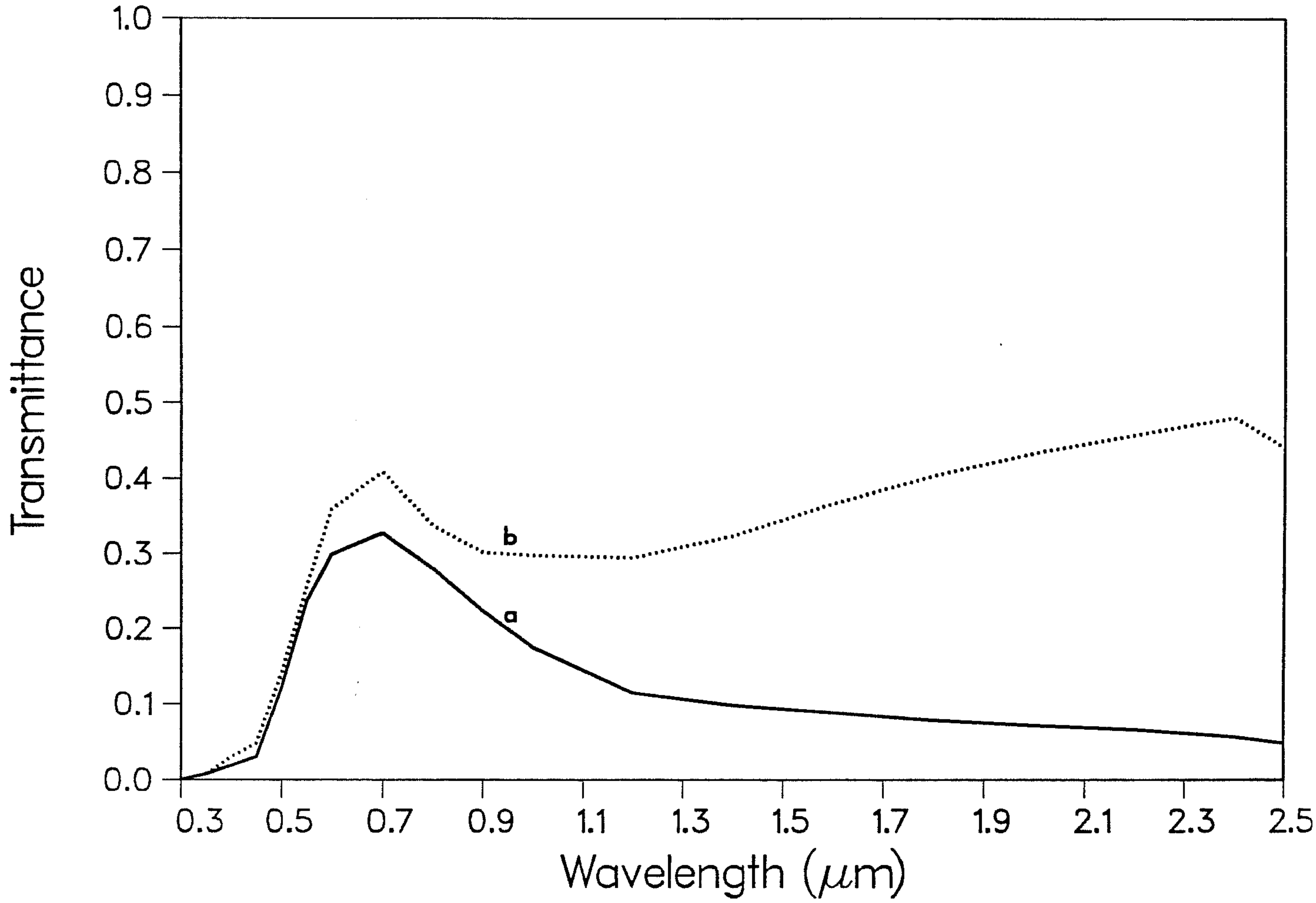

Figure 3. Example of the change in transmittance over the solar spectrum for VO_2 coatings (a) above and (b) below T_t.

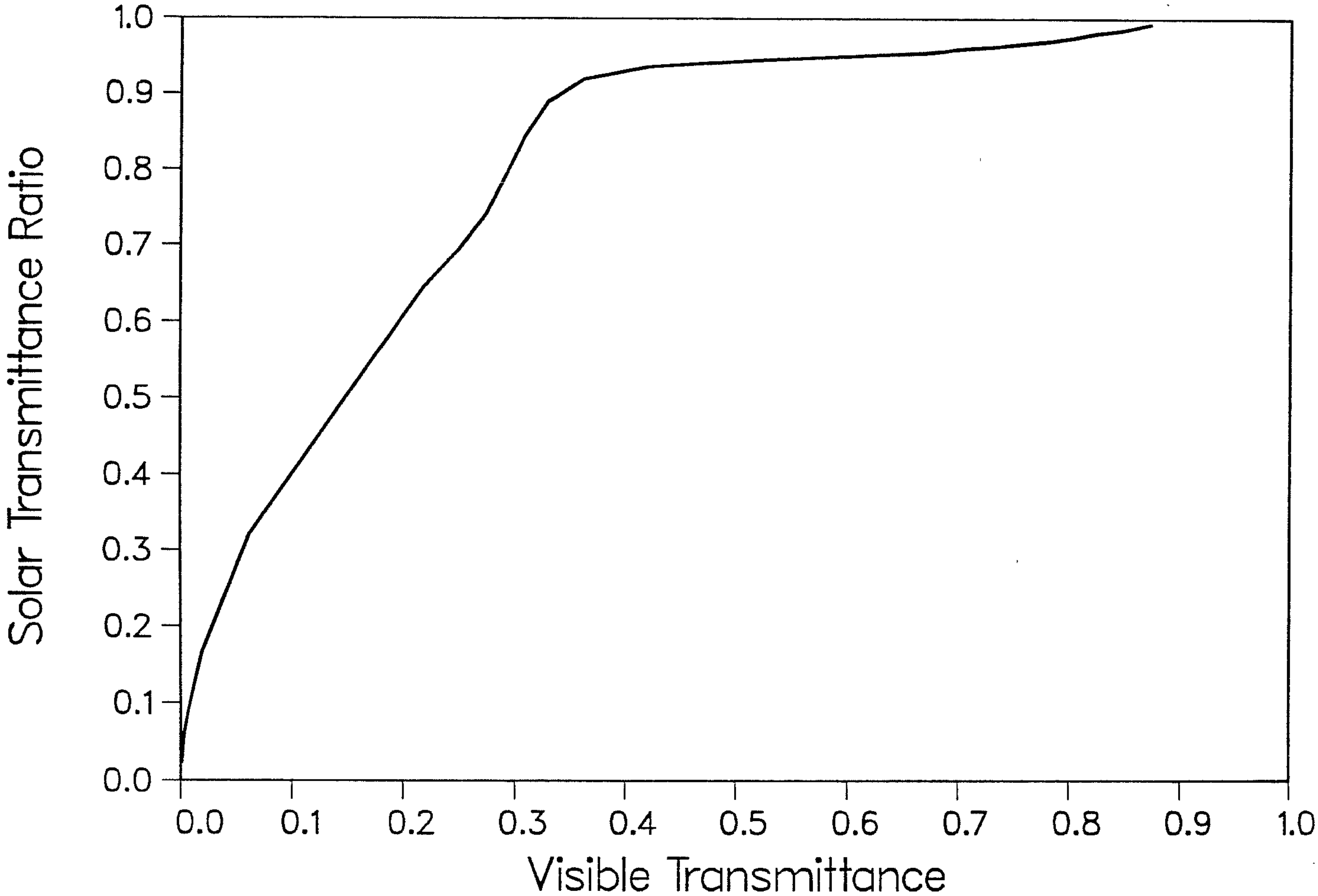

Figure 4. Ratio of the average solar transmittances above and below T_t versus the visible average transmittance above T_t.

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