

A - Sputtered Electrochromic V_2O_5 Films

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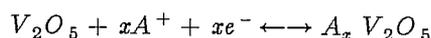
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Abstract

Vanadium oxide films were deposited by reactive dc magnetron sputtering from a vanadium target in argon-oxygen gas mixtures. The composition and structure of these films were investigated by x-ray photoelectron spectroscopy and x-ray diffraction. Films with the approximate composition V_2O_5 were amorphous when deposited at room temperature and had a reversible color change when lithium was electrochemically injected. Because the color change is slight, these films could be used as a counterelectrode to a more strongly coloring material.

Introduction

Electrochemically coloring (electrochromic) materials can be used in electronic displays or in variably transmitting windows. In this paper, we report our findings on the sputter deposition and electrochromic properties of vanadium pentoxide (V_2O_5). This compound is a member of a group of transition-metal oxides that are known to form metallic "bronzes" with variable amounts of another element A. Atoms of A can be added to or removed from the V_2O_5 superstructure through the reaction



where $A = H$ or Li . An oxide that does not have a strong color change under this reaction has the potential to be used as an ion-storage electrode or counterelectrode to the coloring electrode. Goldner and coworkers¹, and Rauh and Cogan² have used V_2O_5 films as counterelectrodes in tungsten trioxide devices.

V_2O_5 films have been deposited by reactive rf sputtering^{2,3}, rf sputtering of V_2O_5 powder⁴, vacuum evaporation^{1,5-7}, and electrochemical deposition⁸. It is important, however, to develop these coatings by methods which conform as closely as possible to standard industrial methods. For this reason, we use dc magnetron sputtering at room temperature which is one of the primary methods used in large-scale glass coating.

In the next section, we describe the deposition and characterization of the films, relating the growth conditions to film composition and structure. We then demonstrate a technique by which the films can be electrochemically colored, and we measure optical properties in both colored and uncolored states.

Film Growth and Characterization

The films investigated here were deposited by reactive dc magnetron sputtering of vanadium in argon and oxygen. The films were made without substrate heating or bias.

The target was a disk of 99.9% V, 75 mm in diameter, bonded to a water-cooled copper backing plate 4 cm above a grounded stainless-steel substrate holder. The substrates were either uncoated glass or SnO₂:F-coated glass. The substrate temperature rose from 22 ° C to less than 60 ° C during deposition.

The sputtering chamber was first evacuated to its base pressure of approximately 10⁻⁶ Torr. Then a mixture of Ar and O₂ was admitted to the chamber. The proportions of Ar to O₂ could be set arbitrarily while the total pressure was held constant by feedback from a capacitance manometer to gas flow controllers. All films were deposited at a total pressure of 10 mTorr, corresponding to a total gas throughput of roughly 145 sccm. The input power was 500 W. A shutter masked the substrates while the target was presputtered.

In reactive sputtering, the flow of reactive gas strongly affects both the discharge and the film. As shown in Fig. 1, the discharge parameters change discontinuously and show hysteresis as the oxygen flow is varied at constant power and total pressure. At low oxygen flow rates, the target surface is essentially metallic, and the depositing film acts as a getter pump for O₂. At high oxygen flow rates, the target surface oxidizes, and gettering is reduced. Films deposited in the metallic-target regime are reflective silver-gray in appearance. Films deposited in the oxidized-target regime are pale yellow. The deposition rate is 2.4 nm s⁻¹ in the metallic-target mode and 1.0 nm s⁻¹ in the oxidized-target mode. For sputtering power between 100 and 500 W, the critical oxygen flow (defined as the right-hand edge of the hysteresis loop in voltage) is proportional to sputtering power, with proportionality constant 0.022 ± 0.001 sccm W⁻¹.

Film composition was studied with x-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer PHI 5300 ESCA spectrometer. In the bulk film material, V and O are essentially the only species present. Other elements (such as Ar) make up less than 0.1

at.%. Our XPS results are summarized in Table I. Atomic concentrations of V and O were measured by the peak area method⁹, using the V 3p and O 1s peaks. The binding energy of the V 2p_{3/2} peak is a measure of the V oxidation state. Published values appear in Table II. Both the peak area and chemical shift data indicate that films made in the metallic-target mode are metallic vanadium with oxygen impurities and films made in the oxidized-target mode are V₂O₅. The chemical shifts suggest that oxide films made with less than 17 sccm O₂ are substoichiometric.

The crystal structure of the films was studied by x-ray diffraction using a Seimens Kristalloflex diffractometer. The metallic films have the b.c.c. vanadium structure¹⁰. Films deposited in pure Ar give a strong (110) peak and a weak (211) peak with an intensity ratio similar to that of a randomly oriented powder. Films deposited at 4.5 sccm O₂ give a weak (110) peak and a strong (211) peak, indicating preferred (211) orientation. The peak widths suggest a grain size on the order of 10 nm. Increasing the O₂ flow above 4.5 sccm causes both peaks to weaken as the grain size shrinks and/or the lattice strain increases. The absence of peaks in oxide films deposited above the sputtering transition indicates that these films are amorphous.

Optical and Electrochromic Properties

Optical properties were measured over the visible and near infrared (300-2700 nm) using a Perkin Elmer Lambda 9 spectrophotometer. Fig. 2 gives the spectral transmittance and reflectance of a V₂O₅ film deposited on uncoated glass. The modulation of the curves is caused by thin-film interference. The yellow color of the films is due to an absorption edge near 500 nm. V₂O₅ has a large refractive index (>2 for visible wavelengths) which could be useful for optimizing the optical properties of a multilayer electrochromic coating.

To demonstrate electrochromism in our films, we deposited V_2O_5 on $SnO_2:F$ -coated glass. These films were grown in 15-20 sccm O_2 and were 60-180 nm thick. The $SnO_2:F$ layer is a transparent conductor with a sheet resistance of $10 \Omega/\square$, and potentiostat leads were connected to this layer. The V_2O_5 films are water-soluble, so 1M LiCl in methanol and 1M $LiClO_4$ in propylene carbonate were used as electrolytes. The work was done in a nitrogen-purged glove box; the films also dissolved if the electrolytes were exposed to the air.

One 180 nm V_2O_5 film was converted to $Li_xV_2O_5$, $x \approx 0.4$, by making it the negative electrode relative to a Ag electrode in 1M LiCl in methanol. This film was then used as a counterelectrode to color and bleach the other films in 1M $LiClO_4$ in propylene carbonate. All the films turned gray when lithium was injected, and changed back to yellow when lithium was removed. The voltage across the two electrodes was swept between ± 1.4 V at 10 mV s^{-1} , producing currents on the order of 0.1 mA cm^{-2} . Charge transfer was 5 to 15 mC cm^{-2} . To do the optical measurements, the sample was rinsed with methanol and dried with nitrogen before removal from the glove box. Open circuit memory of films remaining in electrolyte was on the order of 1 day.

The transmittance change of a $Li_xV_2O_5/SnO_2:F/glass$ sample is shown in Fig. 3. In the colored state, the absorption edge shifts down in wavelength, resulting in the more neutral grey color. The visible average transmittance (weighted by the photopic response of the human eye) changes from 0.75 (bleached) to 0.68 (colored). The solar average transmittance (weighted by an AM2 solar spectrum) changes from 0.63 (bleached) to 0.60 (colored). For comparison, the $SnO_2:F$ -coated glass substrate has a visible average transmittance of 0.81 and a solar average transmittance of 0.70.

Conclusion

V_2O_5 films can be grown by reactive dc magnetron sputtering. This process is compatible with standard industrial technology for depositing window films on glass. When deposited at room temperature the films are amorphous and have an electrochromic transformation when lithium ions are injected or removed. The small variation in transmittance would allow these films to be used as counterelectrodes with other cathodically coloring films having greater changes in transmittance.

Acknowledgments

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Heat Technologies, Solar Buildings Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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TABLE I
XPS RESULTS FOR SPUTTERED FILMS

Oxygen Flow (sccm)	x in V_2O_x	V $2p_{3/2}$ Binding Energy (eV)
0.0	0.4 ± 0.1	512.1
2.6	0.8 ± 0.1	512.1
4.5	1.1 ± 0.2	512.1
6.8	1.3 ± 0.2	512.4
8.1	2.0 ± 0.2	512.5
11.7	5.0 ± 0.4	515.7
16.3	4.7 ± 0.4	515.7
19.4	5.1 ± 0.4	517.0

TABLE II

V $2p_{3/2}$ BINDING ENERGIES REPORTED IN THE LITERATURE^a

Species	V	V ₂ O ₃	V ₂ O ₄	V ₂ O ₅
Binding Energy (eV)	511.5-512.9	513.3-515.7	515.0-516.1	516.6-517.5

^aReferences 5,6,11.

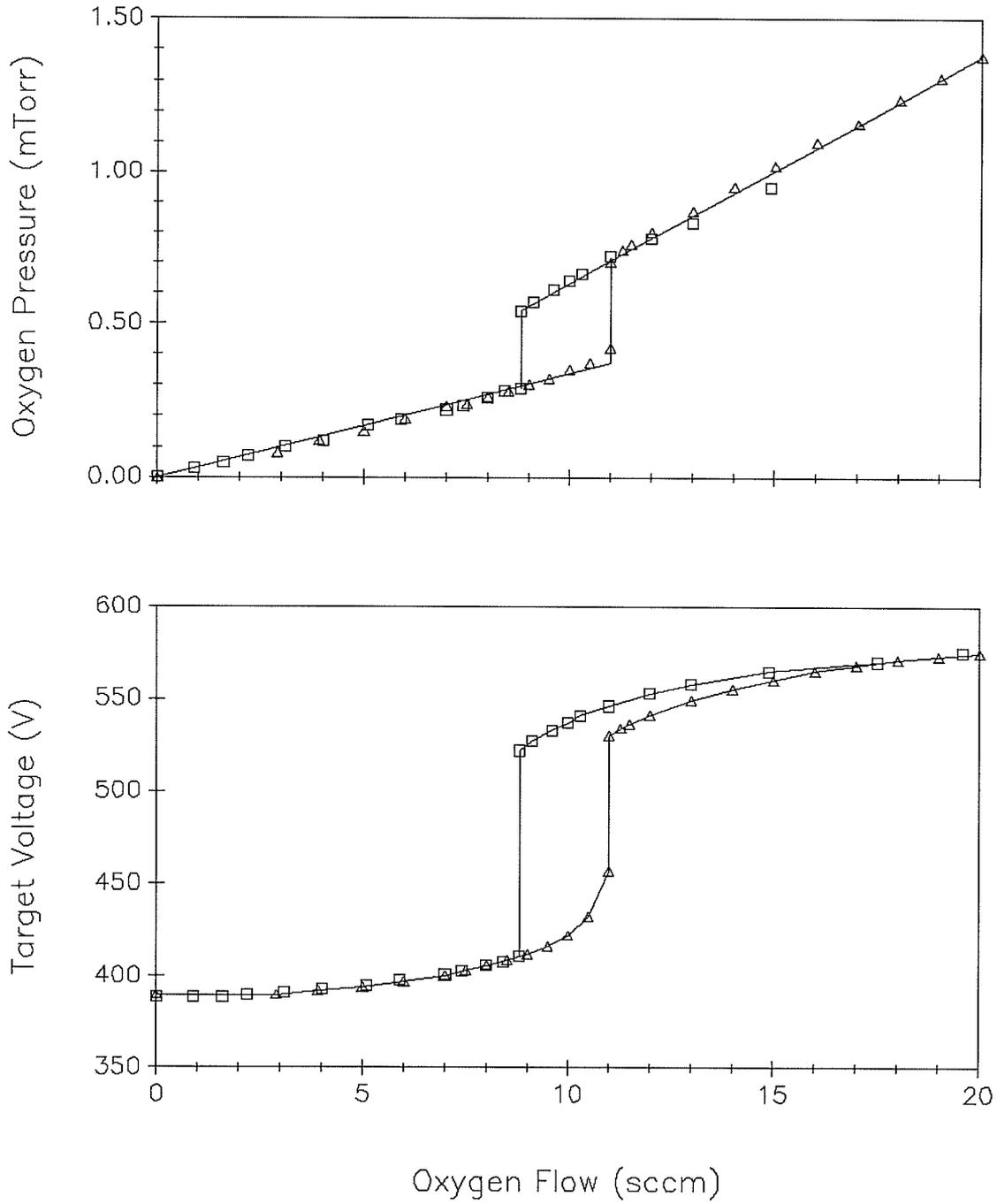
Figure Captions

Fig. 1. Discharge parameters versus O_2 flow for sputtering in Ar and O_2 at 10 mTorr total pressure and 500 W applied power: Δ , increasing O_2 flow; \square , decreasing O_2 flow.

Fig. 2. Spectral transmittance and reflectance of a 230 nm V_2O_5 film on a 1 mm glass substrate.

Fig. 3. Spectral transmittance of a $Li_xV_2O_5/SnO_2:F$ / glass sample in the bleached ($x \simeq 0.0$) and colored ($x \simeq 0.6$) states. The $Li_xV_2O_5$ film was 60 nm thick.

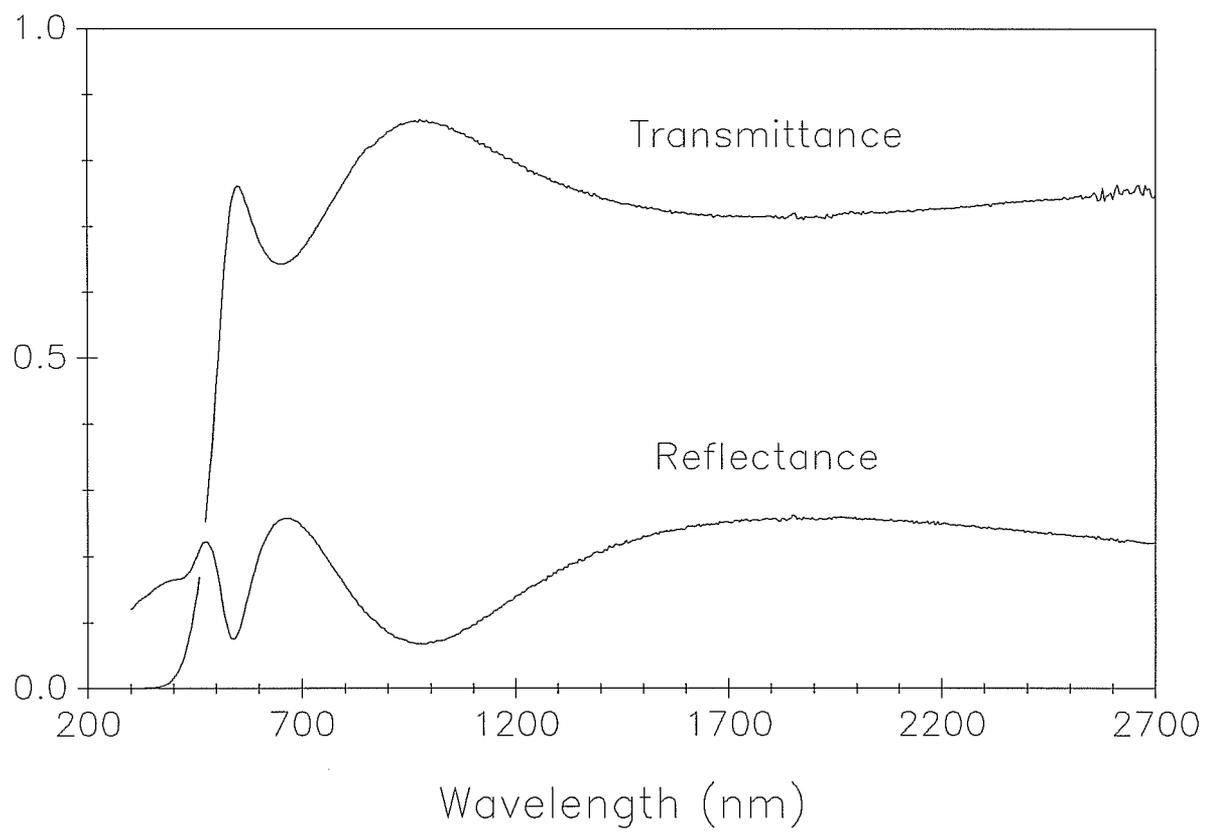
Fig. 1.



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Fig. 2.



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Fig. 3.

