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Chemical and Sonochemical Approaches to the Formation of VO_2 and VO_2-Impregnated Materials

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DISCLAIMER

CHEMICAL AND SONOCHEMICAL APPROACHES TO THE FORMATION OF VO_2 FILMS AND VO_2-IMPREGNATED MATERIALS

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ABSTRACT

A new chemical and chemical/ultrasonic approach to the preparation of VO_2 films and VO_2-impregnated bulk materials has been developed. In this approach, a V_2O_5 sol prepared by quenching is used to coat SiO_2 substrates. The resulting gel-film is heat treated in a reducing atmosphere to form a film identified as VO_2 from the results of X-ray diffraction and both optical and resistivity measurements, which reveal the phase transition characteristic of vanadium dioxide. The advantage of this approach to the formation of VO_2 is that the V_2O_5 sol can be used to impregnate porous materials, which are then heat treated to form an optically active composite material. The switching properties of the VO_2 films are investigated using optical and resistivity measurements, and the results are compared to those obtained for VO_2-films prepared by more-conventional methods.

INTRODUCTION

Vanadium dioxide, both in single-crystal form and as a thin film, has been the subject of a number of previous investigations. These prior studies were motivated by the large variations in the electronic and optical properties of VO_2 that occur as the material undergoes a structural phase transition [1]. This transition is also accompanied by a semiconductor-to-metal transition that is characterized by a change in the VO_2 electrical conductivity of over two orders of magnitude. The phase-transition temperature of ~68°C is sufficiently close to ambient temperature to make this material suitable for a variety of practical applications, including thermally activated optical switching and data storage devices [2,3], modulators and polarizers of submillimeter wave radiation [4], and energy-conserving coatings for windows and walls [5]. Single crystals were found to disintegrate upon cycling through the transition temperature; thin films, however, appear to survive the stresses during repetitive cycles and are, therefore, considered much more practical for applications. High-quality VO_2 films have been obtained using vapor deposition [6], metal oxidation and reactive evaporation [7], reactive sputtering [8], pulsed laser deposition [9], and both organic and inorganic sol-gel methods [10,11,12]. Recently, optically active switchable surfaces have been produced by ion-implantation: by co-implanting vanadium and oxygen into a sapphire substrate and annealing under the proper conditions, it was possible to form buried precipitates of VO_2 [13]. The advantage of this type of active composite surface arises from the fact that the active components are an integral part of the near-surface region of the host material and are, therefore, protected from potential environmental degradation effects.

In this work, a new chemical and chemical/ultrasonic approach to the preparation of VO_2 films and VO_2-impregnated bulk materials has been developed. In this approach, a V_2O_5 sol prepared by quenching is used to coat SiO_2 substrates. The resulting gel-film is heat treated in a reducing atmosphere to form a film identified as VO_2, revealing the switching behavior characteristic of vanadium dioxide. The fact that this approach is a relatively simple and inexpensive way to form VO_2 films makes it very valuable. Its main benefit, however, may lie in the possibility of using the V_2O_5 sol to impregnate porous materials, which can then be heat treated to form an optically active composite material, consisting of VO_2 nanocrystals embedded in the host matrix. Potential candidates for host materials can be found among the so-called sonogels. In contrast to "classic" sol-gels, a sonogel is made without the addition of a solvent. Instead, the different compounds are mixed using ultrasonic energy. Ultrasonic waves propagating through a liquid can generate locally a large amount of energy through the collapse of cavitation bubbles [14]. It has been demonstrated that homogeneous solutions can be formed when 2 immiscible liquids are simultaneously subjected to ultrasound radiation, as a result of the forces acting at their interface. The sonicated water-TEOS solutions quickly gel, giving rise to the so-called sonogels with a superior short gelation time, high density, and a fine, uniform porosity [15]. The surface:volume ratio is typically twice as large as that for gels prepared in an alcoholic solution, which permits sintering at lower temperatures [16]. Sonogels are considered to be superior hosts for nanoparticles and dyes, producing materials with nonlinear optical applications, as well as ceramic composites [17]. The objective of the research effort reported in this paper is to form an optically active composite material, consisting of VO_2 nanocrystals embedded in a silica sonogel.

EXPERIMENTAL DETAILS

In the subject synthesis process, 15 grams of V_2O_5 powder (99.995%, Alfa Aesar, Puratronic) were put in a platinum crucible and melted in air at 1100 °C for 20 minutes. The melt was then poured in 500 ml of distilled water and vigorously stirred. After discarding the residue on the bottom of the jar, a brown sol with approximately 1.6 wt.% V_2O_5 was obtained. Thin films of V_2O_5 were deposited on amorphous SiO_2 substrates (25 x 10 x 2 mm) by dipping the substrates in the sol. A 2-step recipe was used to reduce the V_2O_5 film to VO_2. The first step consists of reducing the V_2O_5 film at 500 °C in argon gas, containing 4 % hydrogen. Under these conditions, the brown film turns gray and converts to mainly V_2O_3. In order to obtain VO_2, a second heat treatment is carried out at 450 °C in argon gas, bubbling through water. The water vapor treatment provides a slightly oxidizing atmosphere, which leads to the formation of a stable blue-colored VO_2 film.

The preparation of the silica sonogels is based on the method of De La Rosa-Fox et al. [15]. In this approach, sonogels are obtained by submitting mixtures of $Si(OCH_3)_4$ (TEOS), H_2O (pH=1) and formamide in a molar ratio 1:10:7 to ultrasonic radiation, produced by a sonifier (Misonix, Model XL2015). Gelling and aging took place at 40 °C.

RESULTS AND DISCUSSION

Figure 1 shows an X-ray θ–2θ scan (using Cu Kα radiation) of a vanadium oxide film formed on a SiO_2 substrate, after being reduced under the conditions described above. The intense peak observed at 27.86° is characteristic of the (011) reflection of VO_2 [18], and suggests, together with the reflections at higher angles, that the film consists mainly of vanadium dioxide. There is, however, at least one impurity phase present, which is difficult to identify because of the large number of nonstoichiometric vanadium oxides that can be formed. Since these oxides could have reflections close to the reflections expected for vanadium dioxide, resistance measurements as well as optical transmission measurements, have been performed in order to confirm unambiguously the presence of VO_2. Figure 2 shows the resistance as a function of temperature for the VO_2 film on the SiO_2 substrate, as the temperature is cycled from room temperature to 100 °C. This figure clearly shows a drastic change in the resistance of the film upon heating and cooling in the 65°-70° C region, i.e. the temperature region where the characteristic VO_2-phase

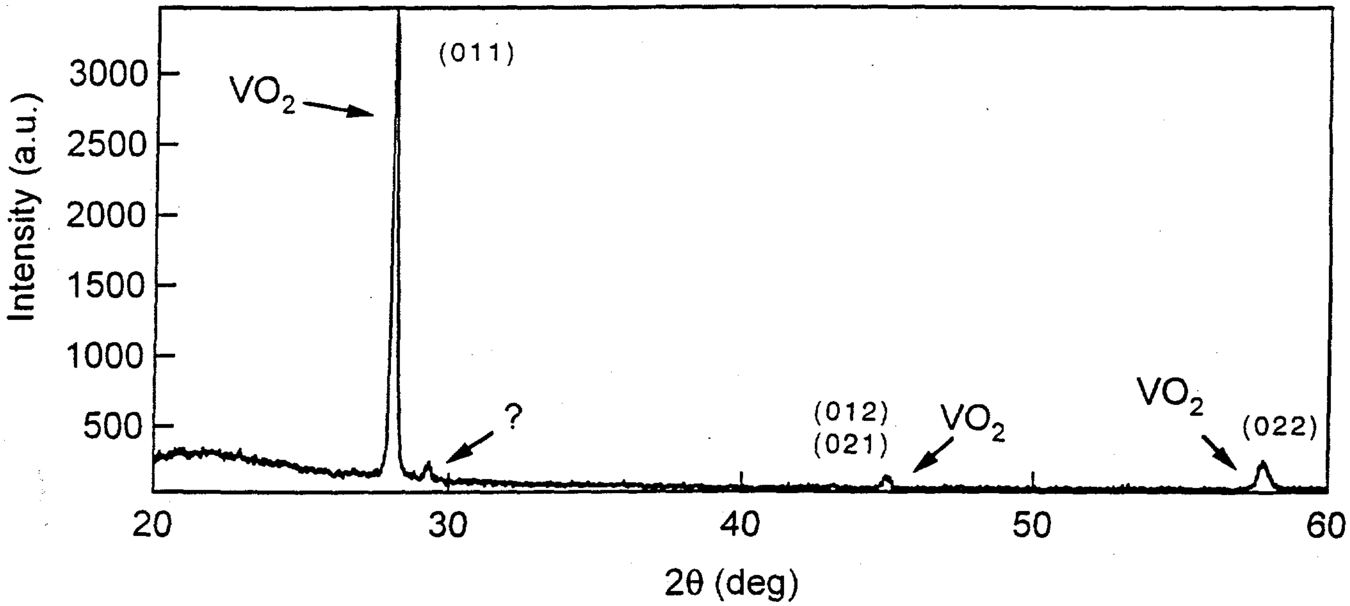

FIGURE 1: X-ray diffraction pattern of a VO_2 film obtained by heat treatment of a V_2O_5 gel-film.

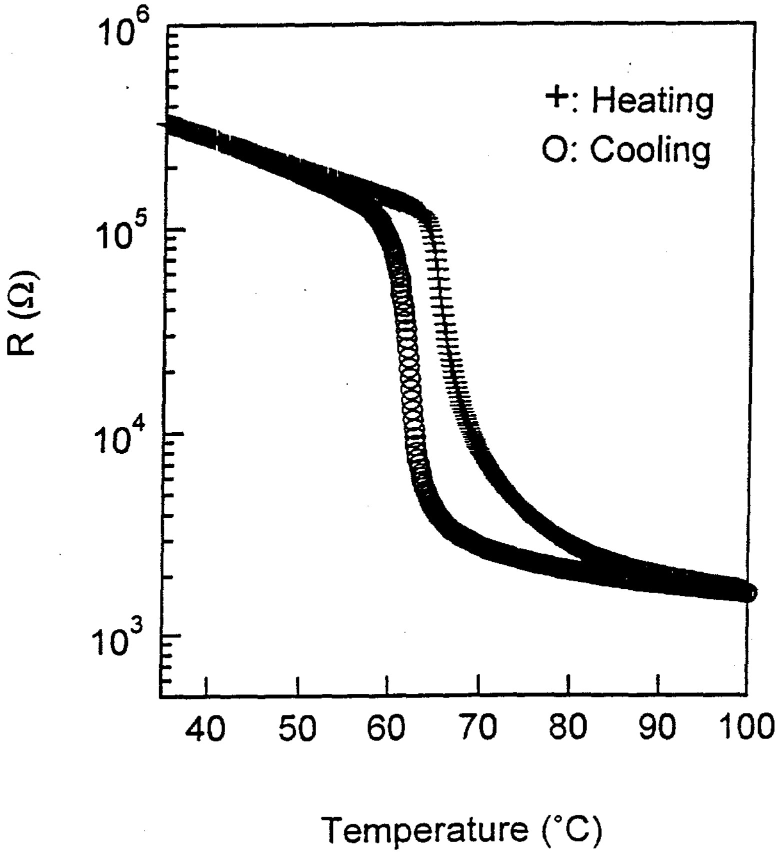

FIGURE 2: Resistance as a function of temperature for a VO_2 film obtained by heat treatment of a V_2O_5 gel-film.

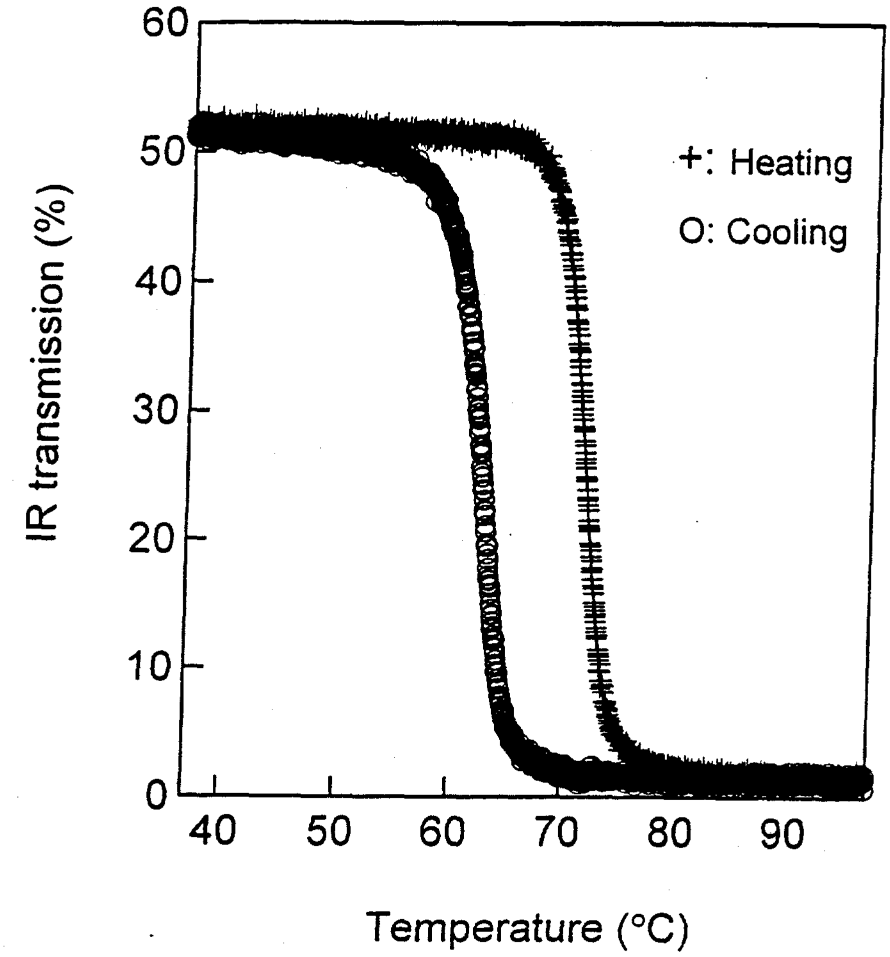

FIGURE 3: IR-transmission ($\lambda = 3.4\mu m$) as a function of temperature for a VO_2 film obtained by heat treatment of a V_2O_5 gel-film. The thickness of the film is approximately 4500 Å.

transition takes place. A change of more than 2 orders of magnitude is observed in our film at a transition temperature of 68 °C, which is typical for films deposited on glass substrates. Although the magnitude of resistive switching has been reported to be between 3 to 5 orders of magnitude for single crystals or thin films on crystalline substrates, it is no more than 2 to 3 orders of magnitude for films on glass substrates [19]. Figure 3 shows the optical transmission for the film, measured at a fixed wavelength of 3.4 μm. It clearly illustrates the drastic change in transmission as the film is cycled through the transition region. Not only is the switching contrast comparable to values reported for "standard" films [20,21], the transition is also remarkably sharp.

The results of this sol-gel approach, as established by the properties of the resulting films, are extremely promising and indicate that superior switching properties may be obtained when the coating-procedure is optimized and the influence of the film-thickness and length of the heat treatments is determined. It will also be interesting to investigate the properties of films deposited on crystalline substrates. However, as noted above, the main benefit of this approach may be the possibility of using a V_2O_5 sol to impregnate porous materials and form thereby "switchable" composite materials. To investigate these possibilities, we have originated a study of silica sonogels as possible hosts for VO_2 nanocrystals. Sonogels were preferred over conventional gels because of their short gelation time and their excellent properties as a host matrix for nanoparticles [17]. One possible way of making such a SiO_2/VO_2 composite is an "in situ" impregnation, where that the V_2O_5 sol can be directly used as one of the compounds to make the sonogel. We were, in fact, able to form homogeneous monolithic gels by adding a V_2O_5 sol to the TEOS-water-formamide mixture. However, in this approach, one has to deal with the fact that V_2O_5 dissolves in formamide, which is used as a drying-control chemical additive (DCCA). Currently, attempts are being made to form homogeneous V_2O_5-containing gels omitting the DCCA or by using another drying-control agent. A second approach to the formation of SiO_2/VO_2 composites consists of "infiltrating" the SiO_2 after gelling. In order to avoid having the V_2O_5 go into solution, the gel-glass has to be sufficiently dry, such that most of the formamide has been removed. Successful infiltration was obtained by soaking the gels, which had been dried at 250 °C, in a diluted V_2O_5 sol. These gels have been subjected to the heat treatments that were found to give the proper reducing condition for the VO_2-films. The first heat treatment, at 500 °C in an Ar/4%H_2 atmosphere changes the color of the film from yellow to gray. This color and the observation that parts of the gel are conducting indicate that the V_2O_5 in the gel has, like the VO_2 films, been reduced to V_2O_3. The second heat treatment, carried out at 450 °C in Argon bubbling through H_2O, returns the gel to its original yellowish color, and no indication of a phase transition around 68 °C could be observed. It is likely that the slightly oxidizing atmosphere, provided by the water vapor, does not supply the right atmosphere for the gel/V_2O_3 system, probably because of the water that is still retained or absorbed by the SiO_2 gel. As a result, a higher oxide is obtained instead of the intended VO_2. Heat treatments under different conditions are currently being carried out in order to find the proper conditions to form a stable SiO_2/VO_2 composite.

CONCLUSIONS

A new chemical and chemical/ultrasonic approach to the preparation of VO_2 films and VO_2-impregnated bulk materials has been developed. In this approach a V_2O_5 sol prepared by quenching is used to coat SiO_2 substrates. The resulting gel-film is heat treated in a reducing atmosphere to form a film identified as VO_2. Resistance and IR transmission measurements as a function of temperature reveal the switching behavior characteristic of vanadium dioxide and indicate that superior switching characteristics may be obtained when the method is optimized. The possibility of using the V_2O_5 sol to impregnate porous materials, which can then be heat treated to form an optically active composite material, has been investigated using silica sonogels as the host matrix. Partially dried gels have been infiltrated with the V_2O_5 sol; however, the heat treatment conditions used to reduce V_2O_5 gel films to VO_2 do not seem to be adequate for the SiO_2 gel/ V_2O_5 system. Future investigations will, therefore, focus on finding the proper reducing atmosphere to form a stable SiO_2/VO_2 composite. Attention will also be paid to the formation and reduction of stable and homogeneous silica/ V_2O_5 composite gels, using the V_2O_5 sol as one of the starting compounds for the sonogel.

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