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Modification of electrical and surface properties of V_2O_3 multilayer films on resin-impregnated highly oriented pyrolytic graphite composite substrates by shrinkage stress relaxation with chemical additives

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ABSTRACT

We investigate the effects of pre-filled acrylic resins in highly oriented pyrolytic graphite (HOPG) substrates on the electrical and interfacial surface characteristics of multilayer films composed of a hexagonal V_2O_3 crystalline phase created by a sol–gel dip-coating process. The films on the resin-embedded HOPG substrates had mud-like shrinkage crack patterns along the grain boundary, with an exfoliated ratio of 0.79%, a thickness increase of 36.79% and a grain size decrease of 21.22%, compared with those of the non-impregnated sample, without changing the intrinsic electrical properties of HOPG. We attribute these results mainly to the use of resins containing hydroxyl groups, which relieve non-uniform drying stresses of the films.

1. Introduction

Crystalline vanadium sesquioxide V_2O_3 has been a very attractive 3-D transition metal oxide compound that exhibits a metal–insulator transition, as described by the Mott–Hubbard physics model [1–3]. It has been previously recognized that crystalline V_2O_3 undergoes a first-order phase transition from an antiferromagnetic insulating phase to a paramagnetic metallic (PM) phase at temperatures below 150 K, with a drastic negative temperature coefficient (NTC) change in electrical resistance accompanied by a distortion of the crystal structure [4–6]. In addition, the phase transition temperature and electrical resistance variation of the crystalline V_2O_3 are known to be seriously affected by process conditions such as temperature, pressure, doping and stoichiometry [7–10]. In recent years, much attention has been paid to investigations of the structural, chemical, optical, and electrical characteristics of nanostructured V_2O_3 films to obtain a theoretically and experimentally deeper understanding of the delicate interplay of the above-mentioned process conditions [11–16]. For high-quality epitaxial growth of the hexagonal V_2O_3 phase in thin films on insulating substrates with a reasonable lattice match (e.g., a-plane (110) and c-plane (001) sapphire), a variety of fabricating and patterning methods have been proposed in the literature: pulsed dc sputtering [17], reactive magnetron sputtering [18], chemical vapor deposition [19], pulsed laser ablation [20], and sol–gel techniques [21,22]. Although a considerable amount of effort has been devoted to exploring the fundamental physical characteristics of V_2O_3 films, moisture-induced stress-related effects on the electrical and surface morphological properties of alkoxide-derived V_2O_3 multilayer films deposited onto electrically conductive porous substrates remain one of the physically recondite subjects.

In this study, we report on the influence of moisture-induced shrinkage stress relaxation on the surface-morphological crack-pattern evolution and the electrical and interfacial characteristics of V_2O_3 multilayer thick films deposited onto the surface of a basal plane of both pure (i.e., non-impregnated) and acrylic resin-impregnated, highly oriented pyrolytic graphite (HOPG) porous substrates. The present research is intended to elucidate the compensation effects of the diffusion of water vapor, formed from the hydroxyl species of impregnated acrylic resins inside the HOPG substrate in V_2O_3 multilayer films, on the relaxation of drying stress gradients, which are induced by the difference in shrinkage rates between interior and exterior surfaces of the multilayer films.

2. Experimental details

The forcible impregnation method of acrylic-based thermosetting polymer resins (composed mainly of 93.3 wt.% of 2-hydroxypropyl

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methacrylate, i.e., $H_2C{=}C(CH_3)COO\ CH_2CH_2OH$, pHPMA) was used to modify the pore surface properties of the HOPG substrates. Subsequently, alkoxide-derived wet gel films, including vanadium species, were prepared from a 0.5 M vanadium alkoxide solution and then deposited onto the flat surface of pre-cleaned and dehydrated 1.4 mm-thick, 10 mm × 10 mm-square non-impregnated HOPG (abbreviated to NONr_HOPG) and resin-impregnated HOPG (abbreviated to IMr_HOPG) substrates. In the present study, the 0.5 M vanadium-containing sol was synthesized by mixing 2-propanol-oxovanadium (i.e., $VO(OPr^i)_3$, Sigma-Aldrich Co. LLC.), 2-propanol (i.e., Pr^iOH, Sigma-Aldrich Co. LLC.), and chelating agents (i.e., acetyl alcohol). The as-prepared vanadium sol was then aged in a cool environment for 72 h before use. Additionally, each HOPG substrate was prepared with polytetrafluoroethylene (PTFE) masking tape on one side and was dip-coated at a withdrawal speed of $5.0\ mm\cdot s^{-1}$ using a programmed DC motor in a hermetic chamber. In all cases, the multilayered V_2O_5 concentrated films were prepared by conducting 20 dip-coating cycles to obtain films more than 1.0 μm-thick (i.e., the critical thickness for film cracking) [23]. After the initial dry oxidation process (conducted using a halogen lamp), the HOPG-supported specimens were heat-treated at 500 °C for 2.5 h, with a heating rate of $3.5\ °C\cdot min^{-1}$ under a vacuum of 1×10^{-4} Torr, to reduce the amorphous dried V_2O_5 gel films to crystalline V_2O_3 films. For the final experimental step, micro-morphological, interfacial, chemical, and electrical properties of the multilayer films were evaluated and compared by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and the 4-point probe technique. The surface micro-morphologies of the films were observed using a JSM 6700F FE-SEM instrument equipped with a 15-kV accelerating voltage. Furthermore, crystalline phases and crystal structures of the multilayer films were identified using a Rigaku RINT-2000/PC X-ray diffractometer with Bragg–Brentano geometry and monochromatic Cu Kα radiation source (λ = 1.5406 Å, 40 kV, 200 mA), where the XRD patterns were acquired in the diffraction angle range of 5° to 90° and within 0.02° of the detection interval in continuous mode. The temperature-dependent electrical properties of both specimens (i.e., V_2O_3/NONr_HOPG and V_2O_3/IMr_HOPG) were carefully measured over a temperature range of −20 to 80 °C by a 4-point probe method using a Keithley 2182A nano-voltmeter and a Keithley 2400 current source meter.

3. Results and discussion

Fig. 1 displays representative FE-SEM images of the surface and cross-sectional morphologies of 20-layered thick films for both V_2O_3/NONr_HOPG and V_2O_3/IMr_HOPG specimens. Fig. 1(a) and (b) shows that similar mud-like shrinkage crack-patterns were observed on the surface of the multilayered films, consisting of the four-sided polygonal fragments with crack junction angles of ca. 90°. There appear to be directional surface patterns in the structure of the crack network (e.g., the fragment-size distribution and crack-tip) due to the crack nucleation and growth at the adhesive interfaces of the two specimens. In Fig. 1(a) and (b), the crack pattern of V_2O_3/NONr_HOPG shows larger fragments with round crack-tips and the inter-laminar fracture (i.e., delamination) of the multilayer films, compared with those of the V_2O_3/IMr_HOPG. It was found that the films of the V_2O_3/NONr_HOPG specimen had an average thickness of 1.67 μm and an exfoliated ratio of 10.97% of the coated area, whereas the films of the V_2O_3/IMr_HOPG specimen had 2.64 μm average thickness and 0.79% exfoliated ratio. The crack growth patterns of the V_2O_3/IMr_HOPG specimen are a consequence of discontinuity of the crack paths, due to local exfoliation of the films, as shown in Fig. 1(a), restricting the dynamics of mud-like crack patterning evolution along the grain boundary, thus

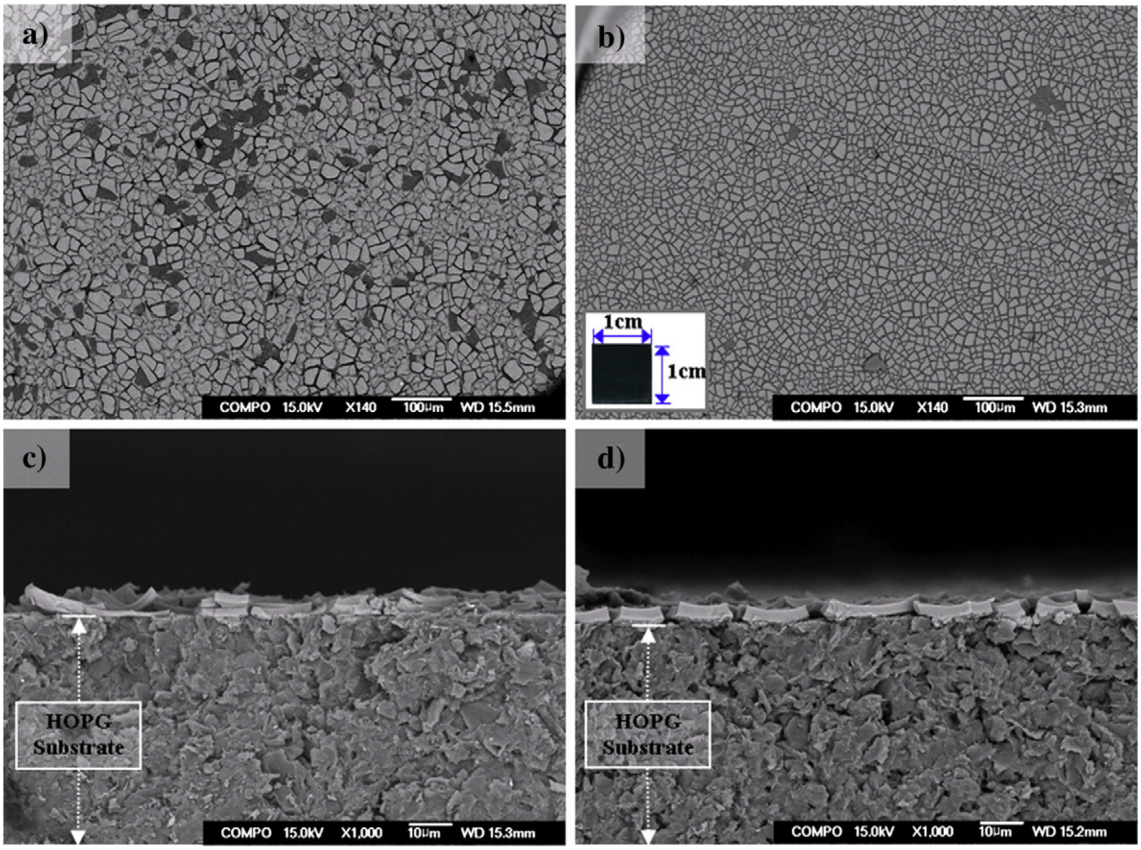

Fig. 1. FE-SEM images of a representative top view of the V_2O_3 20-layered films for both types of samples: (a) V_2O_3/NONr_HOPG and (b) V_2O_3/IMr_HOPG. Additionally, (c) and (d) show a partial cross-sectional view for both the as-synthesized V_2O_3/NONr_HOPG and V_2O_3/IMr_HOPG specimens, respectively.