



High temperature oxidation behavior and mechanical properties of TiAlN/SiN decorative films on borosilicate glass by magnetron sputtering

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ABSTRACT

The coated borosilicate glass is an idea substitute of glass-ceramics in the household electrical appliances due to the rich colors and low cost. By controlling deposition parameters, the black TiAlN decorative film can be fabricated on the borosilicate glass in the magnetron sputtering equipment with multiple chambers. The transparent SiN protective layer also was deposited on the TiAlN film to keep the black color invariant at the high temperature. The TiAlN/SiN films include the inner TiAlN layer with a thickness of 260 nm and the outer amorphous SiN layer with a thickness of 125 nm. The coated borosilicate glass with the TiAlN/SiN films still retains the black color after oxidation at 600 °C in the atmosphere. While the oxidation temperature elevates to 700 °C, the color of the TiAlN/SiN films begins to change. The outer SiN layer plays a role as the barrier against oxygen diffusion into the inner TiAlN layer. The TiAlN/SiN films have a hardness of 15.5 GPa. The oxidation below 600 °C makes the film hardness increase, but the hardness decreases after oxidation at 700 °C. The TiAlN/SiN films have a good adhesion on the glass substrate. After oxidation, the adhesion and toughness of the films decrease significantly.

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1. Introduction

The glass-ceramics are widely used in architecture construction building, household electrical appliances, information and energy field due to their excellent optical, thermal, mechanical and electrical properties [1]. However, the glass-ceramics have a very high cost due to the complex process and high energy consumption. In recent years, many institutes and companies have deposited the decorative films on the surface of the borosilicate glass instead of glass-ceramics to reduce significant costs [2]. The black decorative films on the borosilicate glass have paid more attention due to their widely need in realistic application such as household electrical appliances.

At present in the market, the black ink coating has coated on the surface of the borosilicate glass instead of the glass-ceramics. However, the ink coating has a poor high temperature performance. When the temperature is higher than 450 °C, the ink coating will decompose and this limits its application required in a high temperature environment. Magnetron sputtering is an effective means to prepare functional film on the glass substrate. For example, the thermal control [3–6] and photoelectrical functional films already have many products applied in the market [7–9]. In recent years, the coated glass with the functional

films with special performances has paid more attention in the glass industry. However, there has been the lack of work on the black decorative films, which remain its color stability at a high temperature, on the surface of the borosilicate glass instead of the glass-ceramics [10].

2. Experimental details

The TiAlN/SiN films were fabricated on the borosilicate glass in the magnetron sputtering equipment with multiple chambers. Prior to deposition, the borosilicate glass substrates were cleaned and dried. By optimizing process parameters, the black TiAlN film was fabricated by magnetron sputtering with a large planar TiAl target (100 cm × 50 cm × 5 cm) with atomic ratio of 1:1 for Ti to Al. During deposition, the working pressure was fixed at 0.15 Pa with mixing gases of nitrogen and argon. The black TiAlN film was deposited on glass substrate, and then the coated glass substrate was automatically transferred to the next chamber with Si target to deposit the SiN film, which was employed to protect the inner TiAlN film to remain black even at a high temperature. The TiAlN/SiN films on the borosilicate glass were treated in atmosphere using a tube furnace with double-temperature area at different temperatures (500–700 °C) for 30 min.

Surface and cross-section morphologies of TiAlN/SiN films were observed by scanning electron microscopy (SEM) (Hitachi S4800) with 4 kV of voltage equipped with energy dispersive spectroscopy (EDS) with 15 kV of voltage. The crystallographic structure of the films was

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studied by X-ray diffraction (XRD) (Bruker AXS D8 Advance, made in Germany) with $\text{CuK}\alpha$ radiation in $\theta/2\theta$ mode. The composition and element chemical state were studied by the X-ray photoelectron spectroscopy (XPS) (AXIS UTLTRADLD, made in Japan). The composition and element chemical state were studied by the X-ray photoelectron spectroscopy (XPS) (AXIS UTLTRADLD, made in Japan). The sputtering was performed by an argon ion beam with 2 kV of voltage and 100 μA of current. The working function was calibrated using a silver specimen and the $\text{Ag}3d_{5/2}$ peak positioned at 368.25 eV. Scanning the whole spectrum, to determine element types and then select the energy range of elements to scan again. The peak fit was analyzed by Vision Processing. The background of Shirley was deducted. Gaussian–Lorentzian peaks were used for fit analysis. C_{1s} peak (284.8 eV) is used to calibrate XPS spectra of other elements, i.e. the calibration of XPS peaks has referenced by the change of C_{1s} (284.8 eV). In order to identify the element chemical state, the binding energy of the elements has referenced from the corresponding references. The mechanical properties such as elastic modulus and hardness were measured by a nanoindenter (MTS NANO G200) with a mode of continuous stiffness measurements.

3. Results

Fig. 1a and e shows the top-view and cross-section images of the black TiAlN film on the borosilicate glass. From the top-view images, the TiAlN film is composed of many small particles with a size of several hundred nanometers. The cross-section images show a clear columnar crystals feature with a thickness of 300 nm. Fig. 1b, c and d shows the

morphologies of the TiAlN film after oxidation at different temperatures. After oxidation at 500 °C, the TiAlN film still remains black by visual observation, though SEM top-view images show a slight change of the film. When the oxidation temperature reaches to 600 °C, the color of the TiAlN film has a small change. The oxidation at 700 °C makes the color of the TiAlN film become white. And the top-view SEM image (Fig. 1d) also shows a big change and many pores appear on the surface of the TiAlN film.

In order to improve the color stability of the black TiAlN film at a high temperature, the SiN film was deposited on the surface of the TiAlN film. Fig. 2 shows the top-view and cross-section SEM images of the TiAlN/SiN films. The cross-sectional image reveals that the SiN film has a thickness of about 125 nm. The SiN film plays an important role to improve the color stability of the TiAlN film. After oxidation at 700 °C, the color of the black TiAlN film has not change by visual observation though the morphology of high magnification by SEM shows a slight change. While the oxidation temperature is over 700 °C, the film color has changed from black to light black, and moreover, some film peelings have been found in local surface of the TiAlN/SiN films.

The composition and structure evolution were evaluated by XRD and XPS for the TiAlN/SiN films before and after oxidation. Because the analysis depth is only several nanometers, the XPS spectra reveal the information from the near surface of the SiN film. Fig. 3 shows the XPS survey spectra from the TiAlN/SiN films before and after oxidation. Comparing with the SiN film, oxidation treatment leads to an obvious change of composition, and the content of oxygen and carbon increases, and nitrogen is nearly not detected.

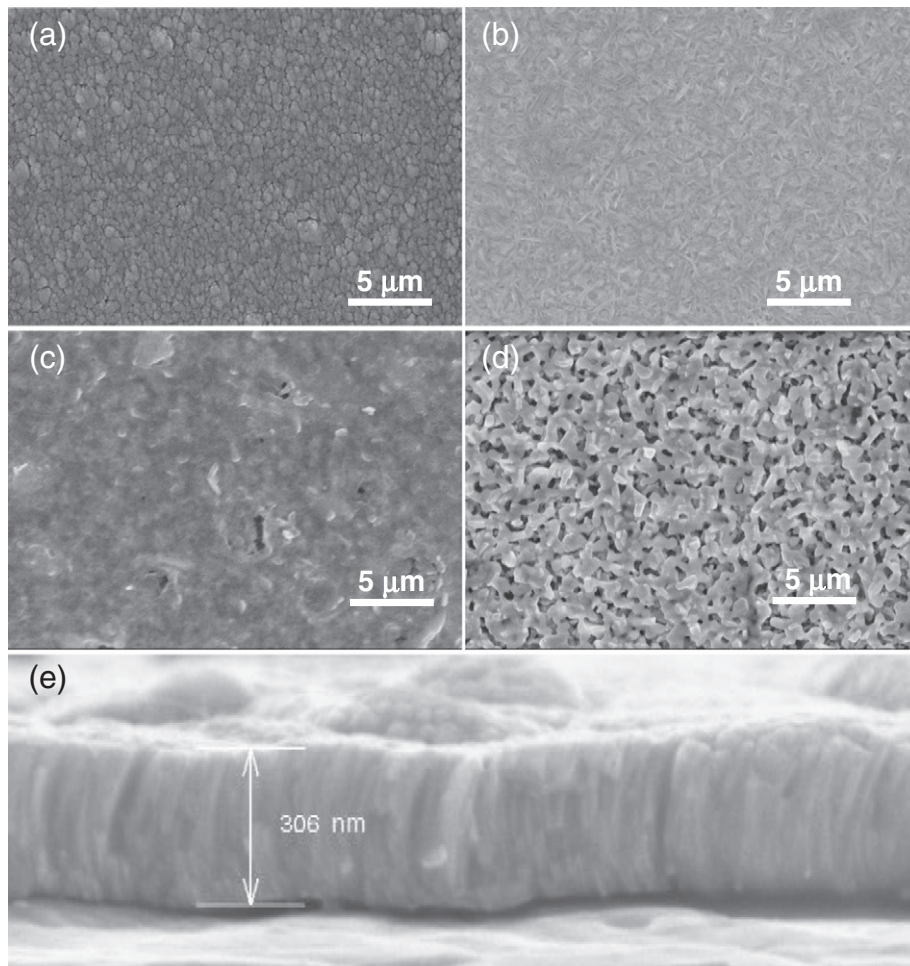


Fig. 1. SEM top-view images of TiAlN films before (a) and after oxidation at (b) 500 °C, (c) 600 °C and (d) 700 °C for 30 min; (e) cross-section images of TiAlN film.

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