Infrared Transparency and Conductivity of Amorphous Ternary Ceramic Thin Films

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Abstract. In this paper, using polycrystalline Ti3SiC2 powder as target, for the first time, amorphous ternary ceramic (a-TSC) thin films are successfully fabricated on quartz and glass substrates at room temperature by direct-current (DC) sputtering. The microstructural and optoelectronic properties of the a-TSC thin films are investigated by means of XRD, Raman, EDS, four-point probe system and Vis-NIR spectrometer, respectively. It is found that despite of amorphous structure and having not so good conductivity compared with Ti3SiC2, the a-TSC thin films still have enough conductivity. Furthermore, compared with ITO, FTO and AZO thin films, the transmittance of a-TSC thin films is much higher in infrared region regardless of the film thickness. It is suggested for a-TSC thin films that the film thickness should be controlled less than 150nm in order to obtain a higher transparency with an appropriate conductivity. It is believed that a-TSC thin film will find its way to be applied in optoelectronic devices in the near future.

1. Introduction

The MAX phases are a unique class of ceramic materials exhibiting favorable properties of both metals and ceramics. MAX phases have a general formula Mn+1AXn and are structurally nanolayered, machinable, ternary carbides or nitrides, in which M is an early transition metal element, A is a group III or IV element, and X is C or N. Like metals, they are thermally conductive [1], thermally shock resistant [2], and relatively damage tolerant [3] because of M-A metal structure [4]. Like ceramics, MAX phases exhibit low densities [2] and oxidation resistance [5]. These MAX phase materials are traditionally applied in structural machine parts, fuel coatings at extreme conditions [6-11]. Up to now, most of the past studies on MAX phase have been focused on tribology and radiation tolerance.

As an exemplar of this materials family, Ti3SiC2 has many great thermal, electrical and mechanical properties [1,12-14]. Whittle et al. [15] studied the radiation tolerance of Ti3AlC2 and Ti3SiC2 using Xe+ and concluded that Ti3AlC2 was more tolerant of radiation damage than Ti3SiC2 due to differences in their electronic orbitals and in their packing efficiency. Recently, autonomous crack healing has been reported for some of the MAX phase ceramics [9] which would contribute to damage reduction. Furthermore, due to the stability of M-X ceramic compound and the mobility of the A element, MAX phases have shown high radiation damage tolerance both experimentally and theoretically. However,
there has been less research on the optoelectronic properties of ternary Ti$_3$SiC$_2$ ceramics. And is it possible to deposit thin films using Ti$_3$SiC$_2$ as raw material in a vacuum chamber? How about the film structure and its optoelectronic properties such as transmittance and sheet resistance?

In this paper, we report the film fabrication of amorphous ternary ceramic thin films named as a-TSC and their structural and optoelectronic properties. The a-TSC thin films were deposited by DC sputtering method using Ti$_3$SiC$_2$ powder as the target. XRD, Raman, EDS, Four-point Probe system and Vis-NIR spectrometer were used to systematically study the structural and optoelectronic properties of a-TSC thin films.

2. Experimental Procedure

a-TSC thin films were deposited on glass or quartz substrates using a direct-current (DC) sputtering system. The substrates were pieces of 15mm×25mm×1.1mm each and cleaned in a sonication bath with acetone and methanol for fifteen minutes. The pieces were then rinsed with deionized water repeatedly and dried by compressed nitrogen. The Ti$_3$SiC$_2$ target, (purity≥98%, 90mm in diameter, and 3–4mm thick) was mounted on a cylinder. The distance between the sample and the target was set to about 8cm. All films were deposited under the same current and nitrogen flow rate at room temperature. The chamber was pumped to a base pressure of $7\times10^{-4}$ Pa, and the current was set to 0.3A. Argon flow served as working gas was kept at 25sccm to keep the chamber pressure in 1.6Pa. The ITO thin film with the thickness of 185nm, FTO 500nm and AZO 500nm were bought for comparison.

A number of techniques were used to analyze the prepared film samples. Panalytical X’pert HighScore XRD instrument was applied to measure the X-ray diffraction spectra, in which a conventional CuK$_\alpha$ radiation ($\lambda=1.5418\text{Å}$) was used, and the angle of incidence was set at 1°. The amorphous network of a-TSC thin films were analyzed by a RENISHAW inVia Raman Microscope at a wavelength of 514nm. EDS results were carried out using a scanning electron microscope (JSM-7500F) with an X-ray energy-dispersive spectra (EDS) attachment. Four-point probe system was used to get sheet resistivity of the film samples, and Idea Optics IS-20-5 spectrometer instrument was applied to study the transmittance of the film samples.

3. Results and Discussion

Fig. 1 shows XRD spectra of a-TSC thin films as deposit, annealed at 500℃ or 800℃, respectively and the insert is the XRD spectrum of ternary ceramic polycrystalline Ti$_3$SiC$_2$ powders for comparison. It can be seen from the insert that the target is polycrystalline and the peaks are consistent with the standard PDF ones. There are no any typical peaks, however, in the XRD spectra of the deposited and annealed thin films, indicating that this kind of thin films are amorphous. It seems that the state of ceramic polycrystalline Ti$_3$SiC$_2$ target sintered at a high temperature is hardly unchanged during the sputtering process. The composition of the deposited films is likely different from that of the Ti$_3$SiC$_2$ target, owing to different departing rates of the three component elements. In order to verify the non-stoichiometric dispersion of Ti, Si and C, EDS was used to analyze the atom weight of the elements upon a SEM instrument as shown in Fig. 2. It is clearly observed that titanium is very little in the a-TSC thin films, and the percentages of all elements are deviated from the stoichiometric ratios of Ti$_3$SiC$_2$ powders. We have tried to crystallize the a-TSC thin films even at an elevated temperature of 800℃, but there are no any diffraction peaks between 2θ=0°–90°. It is accepted that the structure of the a-TSC thin films has been changed considerably through XRD study.

Because of its intensity sensitive to the structural disorder in amorphous thin films, Raman spectroscopy is used to examine our samples besides XRD. A typical Raman spectrum is recorded in the range between 100 and 3000cm$^{-1}$, as shown in Fig. 3. It can be seen that the spectrum has five peaks at around 237, 635, 1362, 1572, and 2776 cm$^{-1}$. It is reported that one can assigns the 635cm$^{-1}$ peak to vibration modes related to the C–Ti–C bonds, and assigns the 237cm$^{-1}$ peak to vibration modes related to the C–Ti–Si bonds [16]. In the range of 100 and 3000cm$^{-1}$, there are other two prominent peaks located at 1362cm$^{-1}$ and 1575cm$^{-1}$, which are associated with the A$_{1g}$ and the E$_{2g}$ vibrational modes of graphite [17,18]. We know that according to the ternary phase diagram [19], carbon is not in equilibrium with
Ti$_3$SiC$_2$, so it is easily understood that the existence of peak 1362 cm$^{-1}$ and peak 1575 cm$^{-1}$ means the deposited film is unlikely crystalline in structure like Ti$_3$SiC$_2$. This result is corresponding to those of XRD and EDS analysis.

![XRD spectra of a-TSC films and Ti3SiC2 powder.](image1)

Figure 1. XRD spectra of a-TSC films and Ti3SiC2 powder.

![EDS results of different samples: (a) a-TSC (45nm). (b) a-TSC (300nm). (c) Ti3SiC2 target.](image2)

Figure 2. EDS results of different samples: (a) a-TSC (45nm). (b) a-TSC (300nm). (c) Ti3SiC2 target.

![Raman spectrum of a-TSC thin film (300nm).](image3)

Figure 3. Raman spectrum of a-TSC thin film (300nm).

Based on the above discussion, we have known that the microstructure of the deposited a-TSC thin films are quite different from that of polycrystalline Ti$_3$SiC$_2$ target. A question is hereby developed that if used as amorphous thin films, are there any superior properties like good conductivity, well erosion resistance and fine antifriction compared with polycrystalline Ti$_3$SiC$_2$? To well answer this question, we have carried out an investigation of film conductivity. For the convenience of observation, the sheet resistance data are logarithmically processed as shown in Fig. 4, and three commercial conductive thin films of ITO, FTO, AZO with certain thickness are chosen for comparison. As the increase of a-TSC films thickness, the sheet resistance generally decreases in the range from ~1300(Ω/□) to 10(Ω/□). Compared with the same thickness of ITO film, the resistivity of a-TSC films is higher than that of ITO film. Taken the thickness as about 500 nm, the resistivity of a-TSC film is almost the same as compared...
with FTO and AZO films. Generally speaking, the a-TSC films still have enough conductivity, which belongs to a higher class of ceramic semiconductor materials and might be useful in some optoelectronic applications.

![Figure 4](image_url)

**Figure 4.** Sheet resistivities of a-TSC films, ITO, FTO and AZO films with different thickness.

In the above-mentioned discussion, we have realized that there still are some C-Ti-C bonds, C-Ti-Si bonds and C-C bonds in the a-TSC films. And it is well known that semiconductor thin films composed of TiC, SiC and DLC (diamond like carbon) are called infrared films owing to their good transparency in this specific band gaps. It is hoped that the deposited a-TSC films could have a good transparency in infrared region. However, up to now, there are few publications on the optical property of a-TSC thin films. Very recently, we have carried out an investigation on the light transmittance of a-TSC thin films in the range of 400–2200nm for the first time. Fig. 5(a) shows the relationship between transmittance and wavelength of 400–2200nm of the deposited a-TSC thin films with different film thickness, compared with the transmittance of ITO film at 185nm, FTO film at 500nm and AZO film at 500nm, respectively. It can be seen that ITO, FTO and AZO films have a higher transmittance of over 80% in visible band, while their transmittance decreases very fast in infrared region. Quite different from above three films, the deposited a-TSC thin films have a much better transmittance from visible even to infrared regions when the film thickness is no more than 150nm. That is to say, compared with ITO, FTO and AZO thin films, a-TSC thin films have an even higher transmittance in infrared region regardless of the film thickness. Fig. 5(b) shows the relationship between transmittance and thickness of the testing a-TSC thin films. It can be seen from Figure 5(b) that the transmittance of a-TSC films decreases with the increase of film thickness. Given a film thickness, it is clearly indicated that a better transparency of a-TSC films moves to a long wavelength. Our suggestion is that to obtain a higher transparency of a-TSC thin film, the film thickness should be controlled less than 150nm.

![Figure 5](image_url)

**Figure 5.** Dependence of the transmittance on the film thickness and wavelength: (a) The transmittance of ITO film, FTO film, AZO film, and a-TSC thin films. (b) The transmittance of a-TSC thin films at different thickness.
4. Conclusion
In summary, amorphous ternary ceramic thin films of a-TSC have been successfully fabricated by direct-current sputtering method. The structural and optoelectronic properties of the a-TSC thin films have been studied by means of XRD, Raman, EDS, Four-point Probe system, Vis-NIR spectrometer, respectively. It is found that compared with polycrystalline Ti3SiC2 target, the microstructure of a-TSC thin films have been changed to amorphous both at the deposition state and at annealed states. Although the a-TSC films are of amorphous and their conductivity are not so good than that of polycrystalline Ti3SiC2, the a-TSC films themselves still have enough conductivity, which belongs to a higher class of ceramic semiconductor materials and might be useful in some optoelectronic applications. Compared with ITO, FTO and AZO thin films, a-TSC thin films have an even higher transmittance in infrared region regardless of the film thickness. It is suggested that to obtain a higher transparency of a-TSC thin film with an appropriate conductivity, the film thickness should be controlled less than 150nm. We believe that a-TSC thin film will eventually find its way to be applied in optoelectronic devices in the near future.

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