Crack Healing Behavior of SiN/SiC Nano-Laminated Films

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Abstract We investigated the self‑crack‑healing behavior of SiN/SiC nano-laminated film. Moreover, we discussed the healing condition including heating temperature and heating time. The films were deposited on a silicon substrate using an ion-beam-assisted deposition. The SiN/SiC nano-laminated film was fabricated with alternating layers of SiN and SiC. After the deposition, a pre-crack was introduced using a Vickers indentor. Then, the cracked samples were heated using an electric furnace in an air atmosphere at the temperature of 600 °C to 1200 °C.

In the case of the SiN and SiC monolayer films, the crack was poorly healed after heating irrespective of the temperature. This was because the size of the crack opening increased after heating. On the other hand, slight crack healing occurred at the temperature of 600 °C. Crack healing improved with an increase in the heating temperature and time. From these results, we concluded that SiN/SiC nano-laminated film has a superior self-crack-healing ability.

Keywords Self-healing, Thin film, Crack, High temperature, Oxidation

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1. Introduction

Ceramic thin films are one of the key materials in micro-electro-mechanical systems (MEMS) such as sensors and micronozzles. Ceramic thin films are superior to metals in terms of strength, heat resistance, and corrosion resistance. However, the sensitivity of these thin films to defects is extremely high and their fracture toughness is much lower than those of metals. The reliability of ceramic thin films decreases significantly once a crack is initiated. Therefore, defects that occur during the deposition and etching process significantly affect the strength and life of MEMS.

For use in MEMS employed under severe conditions such as high temperature or a corrosive environment, ceramic thin films are required to be made more reliable. Self-healing is an important concept for improving the reliability and lifetime of the mechanical components. Recently, various self-healing materials such as polymers, concrete, composites, and coating have been developed by researchers [1–4]. If this ability can be applied to ceramic thin films, then minor defects can be tolerated and cracks caused from the defects during service can be healed before the entire system breaks down.

In bulk materials, certain kinds of structural ceramic composites exhibit self-crack-healing behavior at high temperatures [5–8]. One such composite is silicon nitride (Si_3N_4) reinforced by silicon carbide (SiC) nanoparticles. When a cracked Si_3N_4 composite is heated to a temperature over 800 °C in air, the SiC particles exposed on the crack plane thermochemically react to form silicon dioxide (SiO_2). As this reaction proceeds, the crack is filled by SiO_2, because the volume of SiO_2 expands as compared with that of SiC. The additional SiC plays an important role in the crack healing because of its low reaction enthalpy [8]. Other research groups have reported that a TiC/Al_2O_3 composite coating fabricated by plasma spraying also exhibits self-crack-healing by oxidation in the same manner as that in Si_3N_4 ceramic composites [9].

On the basis of the above reports, it is thought that carbide composite thin films may also exhibit a self-crack-healing ability at high temperatures. In general, thin films for MEMS are fabricated by chemical vapor deposition (CVD) or physical vapor deposition (PVD). However, it is difficult to control the precipitation and dispersion of carbide in these methods. Nanolaminated structures are effective for increasing the crack-growth resistance. Moreover, the crack healing is always induced because a crack can pass the carbide layer surely. In this study, we investigated the self-crack-healing ability of SiN/SiC nano-laminated films at high temperatures. Cracked samples of SiN/SiC nano-laminated films were heated under various heating conditions in air to clarify the factors influencing the self-crack-healing ability of the thin films. In addition, the healed crack was observed and analyzed using scanning electron microscopy (SEM), a focused ion beam system (FIB), and Auger electron spectroscopy (AES) to further analyze the crack healing behavior.

2. Experimental procedures

SiN/SiC nano-laminated films were deposited on Si(100) substrates by ion-beam-assisted deposition (IBAD) [10]. The substrates were cleaned by successive rinsing in ultrasonic baths of acetone. After cleaning, the Si substrates were placed on a water-cooled holder. After the placement of the substrates, the chamber was evacuated to a base pressure of 3×10^{-4} Pa. Prior to deposition, the substrates were sputtered using a nitrogen ion beam at an acceleration voltage of 2 keV for 15 min.

The SiN/SiC nano-laminated films were fabricated with alternating layers of SiN and SiC. The deposition conditions for SiN and SiC are shown in Table 1. The SiN layer was obtained by an electron beam evaporation of silicon (purity: 99.99%) and the simultaneous bombardment of a nitrogen ion beam. The SiC layer was deposited by electron beam evaporation of silicon and simultaneous bombardment of argon ion beam under an ethylene atmosphere at a partial pressure of 2.0×10^{-2} Pa [11]. The fabricated laminated films consisted of four layers and the top layer was SiN. The bilayer thickness was 500 nm. Monolayer films of SiN and SiC were also fabricated in order to compare their properties with those of the SiN/SiC nano-laminated films. The total thickness of all the films was 0.9–1.2 μm.

After the film deposition, a small artificial crack was introduced using a Vickers indenter at a load of 2.0 N. Figure 1 shows an example of the indentation and crack, as observed by field-emission scanning electron microscopy (FE-SEM). A radial crack occurred from the corner of the indentation, as shown in Fig. 1. The cracked samples were heated using an electric furnace in an air atmosphere. It has been reported that the self-crack-healing behavior is dependent on various factors such as heating temperature, heating time, and atmosphere [5]. In this study, the self-crack-healing behavior of the nano-laminated films was investigated systematically by changing the heating temperature

Table 1. Deposition conditions.

	SiN	SiC
Arc voltage (V)	80	
Ion beam	Nitrogen	Argon
Gas flow rate (sccm)	4.0	1.5
Acceleration voltage (keV)	2.0	0.3
Deceleration voltage (keV)	0.3	1.0
Acceleration current (mA)	14.0	15.0
Atmosphere gas	-	Acetylene
Vapor rate (nm/s)	0.2	0.1

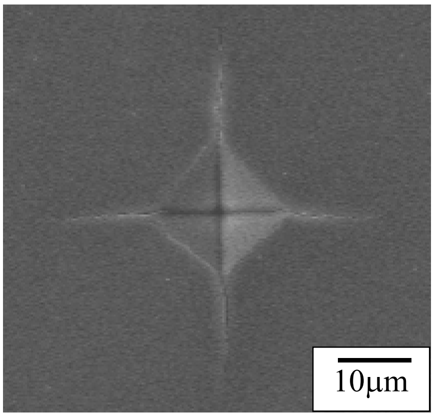


Figure 1. FESEM image of indentation and cracks on SiN film.

(T_h = 600–1200 °C) and time (t_h = 24 h, 48 h, 72 h).

The surface morphology and cross section of the samples were examined by FE-SEM. The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS). AES was used to observe the distribution of the oxides generated by crack healing. Before both analyses, Ar ion sputtering at an acceleration energy of 3 keV was conducted for 10 s to remove any contamination.

3. Results and discussion

3.1 Film morphology

Figure 2 shows the FE-SEM images of the surface and cross section of the deposited films. All films had an extremely smooth morphology. Although the interface between SiN and SiC can be observed, a columnar structure was not observed. Moreover, X-ray diffraction peaks could not be observed. On the basis of these results, it is suggested that the SiN and SiC films fabricated in this study were amorphous.

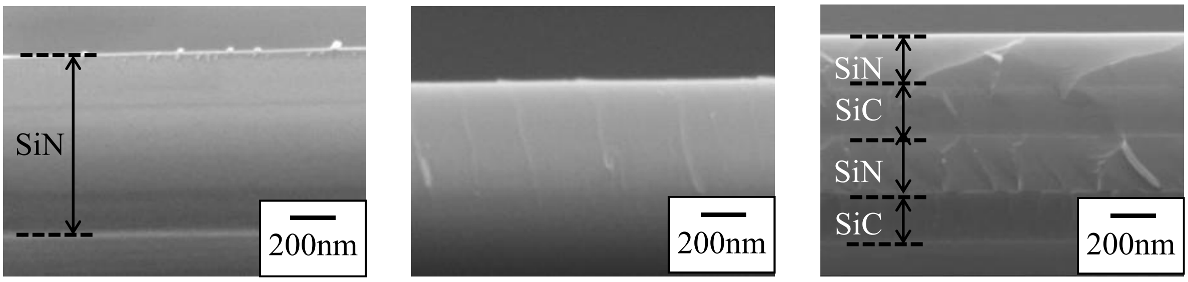
3.2 Chemical composition

The average chemical compositions obtained by XPS analysis are summarized in Table 2. Both films contained some oxygen atoms. It is postulated that the water vapor evaporated during the heating with the electron beam might have been entered the film. Therefore, it is suggested that the SiN and SiC films include some oxide compounds, most probably, SiO_2.

3.3 Crack healing behavior

3.3.1 Effect of film structure

Figure 3 shows the FE-SEM images of the indentation and crack after heating the samples at a temperature of 800 °C for 24 h. In the case of the SiN and SiC monolayer films, the crack was poorly healed after heating, as shown in Figs. 3(a) and (b), respectively; however, a slight crack healing did occur near the crack tip. Moreover, the size of the crack opening increased after heating. When SiN_x and SiC are heated in air, oxidation occurs by the following chemical reactions:



(a) SiN film (b) SiC film (c) SiN/SiC film

Figure 2 FE-SEM images of cross section of thin films.

Table 2. Chemical composition of SiN and SiC film.

Film	Si	N	C	O
SiN	59.6	25.1	–	15.3
SiC	62.7	–	16.2	21.1

$$2\mathrm{SiN}_x + 2\mathrm{O}_2 \rightarrow 2\mathrm{SiO}_2 + x\mathrm{N}_2 \quad (1)$$

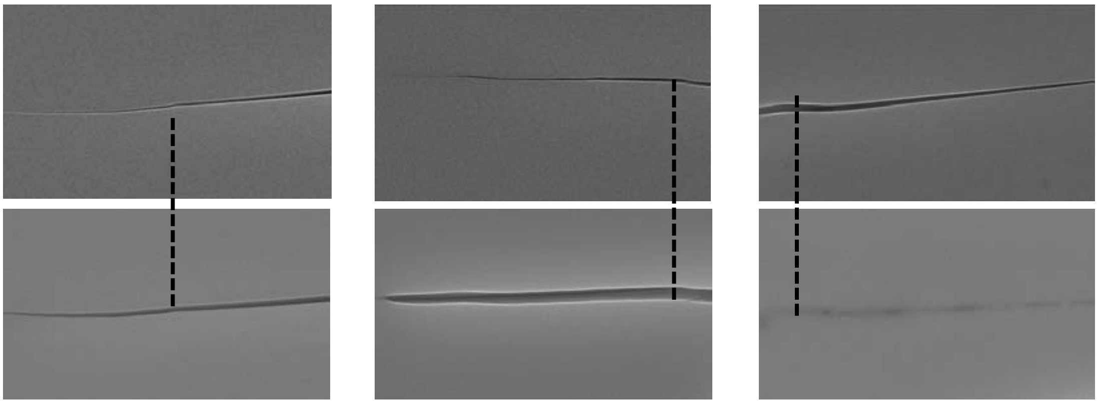
$$\mathrm{SiC} + 3/2\mathrm{O}_2 \rightarrow \mathrm{SiO}_2 + \mathrm{CO} \quad (2)$$

These chemical reactions results in volume expansion, and thereby, crack healing. In the case of the SiN and SiC monolayer films, it was concluded that the crack healing did not occur sufficiently because the volume of the crack-opening region was larger than the volume expansion due to the oxidation reaction.

On the other hand, the cracks in the SiN/SiC nano-laminated films were healed without an increase in crack opening, as shown in Fig. 3(c). The laminated structure probably decreases the residual stress. Delamination was observed around the indentation, which occurred during the heating because the delamination cross section was covered with oxidation products.

Figure 4 shows the FE-SEM image of the cross section of the healed crack. The cross section was achieved using a focused ion beam system. The crack reached the substrate through the film. It was found that the crack in the film was also healed internally. Moreover, the laminated structure was still preserved, which suggests that the oxidation reaction occurred only on the crack plane exposed to air.

The oxide distribution around the indentation and cracks after heating was analyzed using AES. Figure 5 shows a mapping image of oxygen around the indentation and cracks. The Auger electron counts for oxygen were high along the healed crack. It is suggested that the oxidation reaction induced crack healing similar to the healing of bulk Si_3N_4/SiC composites. These results indicate



(a) SiN film (b) SiC film (c) SiN/SiC film

Figure 3. FE-SEM images of crack tip before and after heating. The upper and below images indicate crack before and after heating, respectively. The dotted lines indicate the same points before and after heating.

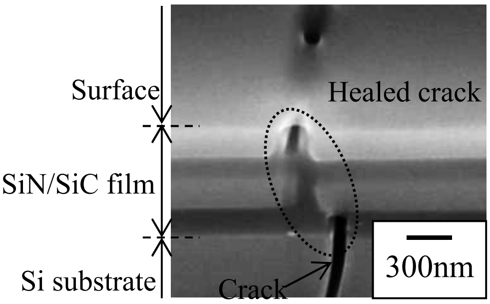
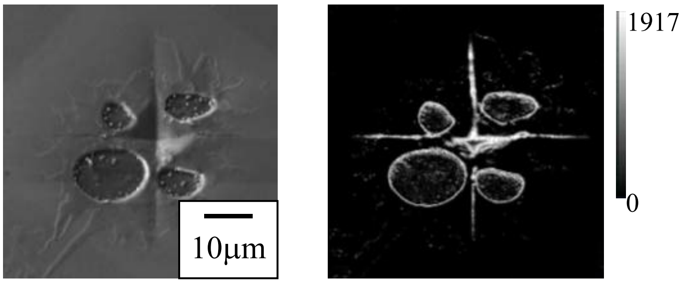


Figure 4. FE-SEM image of cross section of healed crack.



(a) SEM image (b) Oxygen mapping image

Fig. 5 SEM and AES mapping image of oxygen after heating.

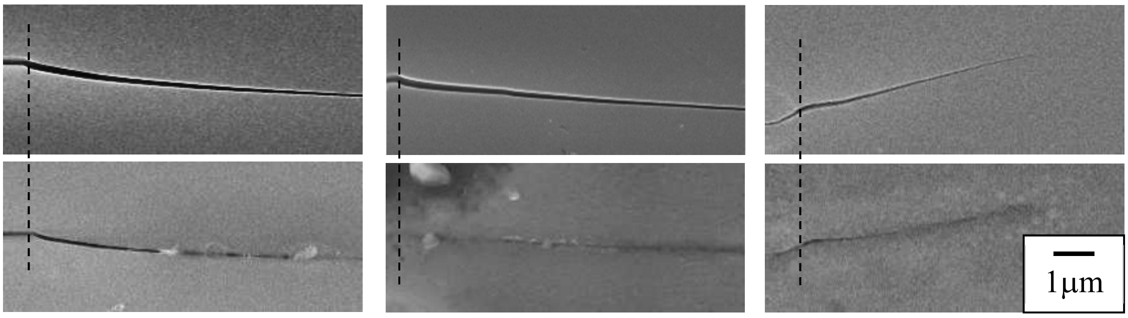
that the self-crack-healing ability of a SiN/SiC nano-laminated film is superior to that of a monolayer film.

3.3.2 Effect of heating temperature

The influence of heating temperature on the self-crack-healing behavior was investigated. The heating temperature was varied from 600 °C to 1200 °C and the heating time was fixed at 1 h. Figure 6 shows the FE-SEM images of the indentation and cracks after heating. Slight crack healing occurred at the temperature of 600 °C. Crack healing improved with an increase in the heating temperature, and heating at 1000 °C healed the crack perfectly. However, at 1200 °C, observation of the cross section and analysis of the chemical composition revealed that even though the crack was healed, the laminated structure disappeared because of oxidation. This indicates that the crack healing ability also disappears once the SiN/SiC nano-laminated film is heated to temperatures over 1200 °C.

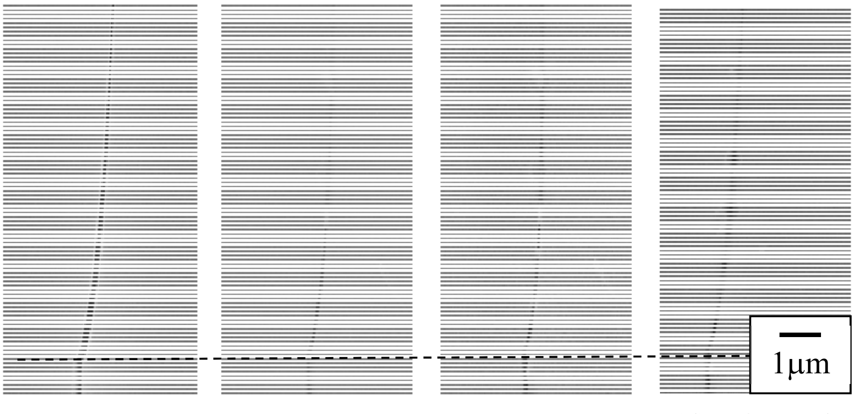
3.3.3 Effect of heating time

The influence of heating time on the self-crack-healing behavior was also investigated. The heating time was varied from 24 h to 72 h at the heating temperature of 600 and 800 °C. Figure 7 shows the FE-SEM images of the indentation and cracks after heating. At 600 °C, crack healing improved with an increase in the heating time. However, at temperatures over 800 °C, the influence of heating



(a) 600 °C (b) 1000 °C (c) 1200 °C

Figure 6. Influence on heating temperature on the crack healing. The upper and below images indicate crack before and after heating respectively. The dotted lines indicate the same points before and after heating.



(a) Before heating (b) After 24h (c) After 48h (d) After 72h

Figure 7. Influence on heating time on the crack healing. The dotted lines indicate the same points before and after heating.

time on the crack healing was not observed clearly. It was postulated that the oxidation reaction on the crack plane was almost completed at 24 h at temperatures over 800 °C because the crack plane exposed to air is extremely small in the case of a thin film.

4. Conclusions

In this study, we investigated the self-crack-healing ability of SiN and SiC monolayer films and SiN/SiC nano-laminated thin films subjected to high temperatures in an air atmosphere. We also analyzed the influence of heating temperature and heating time on the healing ability of the nanolaminated thin films. The investigation yielded the following conclusions:

1. In SiN and SiC monolayer films, cracks were poorly healed because the size of the crack opening increased significantly during heating. On the other hand, SiN/SiC nano-laminated films exhibited a superior self-crack-healing ability.
2. Around the healed crack, the oxygen concentration was found to be high. This indicates that crack healing was achieved by oxidation.
3. Crack healing was promoted by an increase in the heating temperature and time. However, at temperatures over 1200 °C, the laminated structure disappeared and the film was subjected to oxidation overall.

Acknowledgements

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