Development of a wurtzite (Al,Ti)N thermistor on a resin substrate with high heat resistance

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We developed a thin-film nitride thermistor on a resin substrate with high heat resistance by focusing on the interface between the polyimide (PI) substrate and (Al,Ti)N film. Heat resistance properties of nitride thermists are degraded by an amorphous oxynitride layer on the PI substrate that forms during the initial stage of sputtering. We propose the introduction of an inorganic insulating underlayer at the interface between (Al,Ti)N and the PI substrate to prevent the formation of the amorphous phase. As a result, highly crystalline (Al,Ti)N was grown directly on an inorganic insulating underlayer and high heat resistance was achieved.

Key-words : NTC thermistor, Wurtzite nitride film, Reactive sputtering, Laminated structure, High heat resistance

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1. Introduction

Thermistors are widely used as temperature sensors in electronic devices such as smartphones and personal computers, home appliances such as air conditioners, and automobiles. A thermistor is an electronic component that detects temperature as a change in electrical resistance with temperature. Thermistors with negative resistivity are called negative temperature coefficient (NTC) thermistors, and the electrical resistance $R$ of an NTC thermistor is represented by the following Arrhenius equation:

$$R = R_0 \exp \left\{ B \left( \frac{1}{T} - \frac{1}{T_0} \right) \right\}$$  \hspace{1cm} \text{(1)}$$

where $T_0$ is the reference temperature and $R_0$ is the resistance value at the reference temperature. Normally, the reference temperature is 25 °C. The material properties corresponding to the activation energy are defined by the $B$ constant. The $B$ constant is evaluated by measuring the electrical resistance values at different temperatures. The temperature coefficient of the resistance value can be expressed as $B/T^2$, and the $B$ constant is used as an index of the temperature detection accuracy of an NTC thermistor.

In recent years, the need for high-speed thermal response in order to control the temperature of various electronic devices with higher temporal accuracy has been increasing. Both thinness and flexibility for measuring in narrow and curved space are demanded. Therefore, we developed a thin-film thermistor deposited on a resin film substrate. Polyimide (PI) were selected as resin substrate, which has both high heat resistance and mechanical strength. This substrate is thin and has small heat capacity so that the sensor can follow the temperature change of the heat source.

Conventionally, spinel-type oxides and perovskite-type oxides are widely used as thermistor materials. However, oxide ceramics are difficult to deposit on a resin substrate due to their high crystallization temperature. We therefore focused on AlN-based materials that can be deposited as tough thin films by sputtering at low temperatures. AlN is used as an electronic material in various applications such as piezoelectric devices and heat sink modules. However, in order to apply AlN-based nitride as thermistor material, Al needs to be replaced with a transition metal to create conductive carriers because AlN is highly insulating due to a wide band gap of 6.2 eV.

Wurtzite (Al,Ti)N thin films are directly deposited on PI substrate by reactive sputtering. The fabricated (Al,Ti)N films on PI substrate have a total thickness of less than 100 μm and are flexible enough to fit on round surfaces such as batteries and also offer high-speed thermal response.

Another important property of film thermistors is high-temperature heat resistance. This study analyzed the initial crystal growth of (Al,Ti)N, and elucidated the essential properties for high heat resistance. From the results, the insertion of an inorganic insulating layer between the PI substrate and (Al,Ti)N thin film was found to be effective for improving the heat resistance. Excellent heat resistance...
was thus achieved in a thin-film thermistor employing a resin substrate.

2. Experimental procedures

2.1 Sample preparation

PI substrate of thickness 50 \( \mu \text{m} \) was dried at 150 °C for 30 min in air to remove moisture from the surface before sputtering. \((\text{Al}_{0.85}\text{Ti}_{0.15})\text{N}\) thin film of thickness 100 nm was then deposited on the PI substrate by RF magnetron reactive sputtering. \((\text{Al},\text{Ti})\text{N}\) sputtering was carried out in \(\text{N}_2/\text{Ar}\) mixed gas at 0.2 Pa after vacuuming below \(4 \times 10^{-5}\) Pa. In the sputtering process, the input power was 200 W and the PI substrate was not heated. The substrate temperature was confirmed to be below 40 °C by thermo label.

The internal stress between \((\text{Al},\text{Ti})\text{N}\) and PI substrate was controlled by adjusting \(\text{N}_2/\text{Ar}\) ratio. Then, appropriate compressive stress was induced on \((\text{Al},\text{Ti})\text{N}\) film. Delamination and cracks were not observed in \((\text{Al},\text{Ti})\text{N}\) film even after heat resistance test, despite the deference in thermal expansion coefficients between \((\text{Al},\text{Ti})\text{N}\) and PI substrate. After sputtering, the \((\text{Al},\text{Ti})\text{N}\) film was formed by a wet etching process. Cr and Au electrodes were then deposited by sputtering, with these electrode forming comb-shaped electrodes on the \((\text{Al},\text{Ti})\text{N}\) layer by wet etching [Fig. 1(a)].

Figure 1(b) shows an inorganic insulating underlayer inserted between the PI substrate and \((\text{Al},\text{Ti})\text{N}\) thin-film. Crystalline AlN, amorphous AlOx, and amorphous SiNx were selected as the underlayer, which was deposited by reactive sputtering using targets of each constituent element. Sputtering of underlayers was carried out in \(\text{N}_2/\text{Ar}\) mixed gas from 0.1 to 0.7 Pa after evacuating the sputtering chamber to below \(4 \times 10^{-7}\) Pa. The input power was varied from 100 to 500 W. Similarly, this underlayer was deposited with appropriate compressive stress without delamination and cracks.

2.2 Characterization

The crystal structure of the \((\text{Al},\text{Ti})\text{N}\) thin film was determined by X-ray diffraction using Cu-K\(\alpha\) radiation.

Cross-sectional textures were observed by TEM and STEM using samples processed by focused ion beam. The composition of the cross-sectional textures was measured by energy-dispersive X-ray spectroscopy (EDX).

Heat resistance was tested at 260 °C in air. The thermistor element was held at a high temperature for 2000 h in a furnace, and then the electrical resistance was measured at 25 °C. The change in electrical resistance was evaluated as \(\Delta R_{25}\) (%). The target value of \(\Delta R_{25}\) is expected to be within ±5 % after 2000 h of testing. Meanwhile, the resistivity of inorganic underlayer is much higher than that of \((\text{Al},\text{Ti})\text{N}\) film, and it affect little to the resistance change of thermistor.

3. Results

3.1 Analysis of PI/(\text{Al},\text{Ti})\text{N} interface

X-ray diffraction measurement confirmed that \((\text{Al},\text{Ti})\text{N}\) has a single phase of the Wurtzite crystal structure (hexagonal crystal, space group \text{P6}_3\text{mc}) and has high c-axis orientation perpendicular to the substrate. Similar results were also obtained on other substrates such as SiO\(_2\) on Si and glass substrates. In addition, electron diffraction patterns from TEM also indicated that \((\text{Al},\text{Ti})\text{N}\) has a high c-axis orientation perpendicular to the substrate. Figure 2 shows a cross-sectional TEM image of the thermistor element without underlayer before heat resistance test. Columnar crystalline films of \((\text{Al},\text{Ti})\text{N}\) are formed on PI, and Cr/Au electrodes are formed on \((\text{Al},\text{Ti})\text{N}\) without any defects. Figure 3 shows a cross-sectional TEM image and EDX oxygen mapping image focused on the PI/(\text{Al},\text{Ti})\text{N} interface before heat resistance test, which shows that a thin oxynitride layer was formed just above the PI, and since no lattice fringes were observed from oxynitride layers, the oxynitride layer is amorphous. This amorphous layer formed only during the initial stage of growth, and then \((\text{Al},\text{Ti})\text{N}\) crystal nuclei formed on the amorphous layer which gradually grew into columnar crystals. It is thought that the incorporation of oxygen contained in PI promoted the formation of an amorphous layer during the initial growth. Moreover, X-ray Photoelectron Spectroscopy shows that amorphous oxynitride layer oxidizes...
during heat resistance test. It is possible that this oxidation of an amorphous layer due to oxygen diffusion from PI substrate had a large effect on degradation of the thermistor element’s heat resistance.

3.2 Introduction of inorganic insulated underlayer

An inorganic insulated underlayer was deposited on the PI substrate to suppress formation of an amorphous (Al,Ti)N layer during the initial growth. The underlayer needs to have much higher resistivity than the (Al,Ti)N film in order to main both electrical resistance value and $B$ constant. Therefore, crystalline AlN, amorphous AlO$_x$, and amorphous SiN$_x$ are proposed as potential underlayers in this work. The crystallinity of the underlayer was identified by X-ray diffraction and TEM electron diffraction.

Figure 4(a) shows a cross-sectional TEM image of the entire thermistor element with AlN underlayer and Fig. 4(b) shows an image focusing on the interface between the AlN underlayer and (Al,Ti)N layer. Columnar crystal grains grew directly on AlN without the formation of an amorphous oxynitride layer during initial growth.

(Al,Ti)N has the same wurtzite crystal structure as AlN, and the lattice constant on the $a$-axis direction has a slight difference of only 1.5%. Therefore, high crystallization of (Al,Ti)N on the AlN underlayer was expected.

Figures 5 and 6 show cross-sectional TEM images of thermistor elements with an amorphous AlO$_x$ underlayer and amorphous SiN$_x$ underlayer, respectively. Even though both underlayers were amorphous, (Al,Ti)N columnar crystal grew directly on the underlayers without forming an amorphous layer. As a result, the crystallinity of (Al,Ti)N during the initial growth was much improved by inserting an underlayer regardless of crystallinity and composition of the underlayer. The inserted underlayer prevented (Al,Ti)N from taking oxygen from the PI substrate, which suppressed the formation of amorphous oxynitride and promoted crystal growth of (Al,Ti)N during the initial stage.

Meanwhile, amorphous oxynitride layer was not formed on SiO$_2$ on Si, even though SiO$_2$ contained oxygen as well as PI substrate. We considered that oxygen does not diffuse from inorganic substrate since the bonding energy of oxygen atom to metal atom in inorganic oxide is much higher than that in PI substrate.

3.3 Results of heat resistance test

Figure 7 shows the change in the heat resistance at 260 °C in thermistor elements with and without crystalline AlN-underlayer. The thickness of AlN underlayer is 50 nm. The $\Delta R_{25}$ of the thermistor element with underlayer after 2000 h was 3.0 %, while the $\Delta R_{25}$ of the thermistor element without underlayer was 6.6 %. The change in the resistance of the thermistor element with AlN-underlayer was much improved compared to the target value of $\Delta R_{25}$ within ±5%. We thus successfully developed a thermistor sensor with high heat resistance using a resin substrate.

Figure 8 shows the results of 260 °C heat resistance tests on thermistor elements with different types of amorphous underlayers AlO$_x$ (50 nm) or SiN$_x$ (50 nm) on PI substrate, and SiO$_2$ (500 nm) on Si substrate. The $\Delta R_{25}$ values for the thermistors with amorphous underlayer were lower than without the underlayer. In addition, these $\Delta R_{25}$ values are almost the same as the results of using a crystalline material as the underlayer as shown in Fig. 7. We confirmed from other measurements that the $B$ constant remained almost unchanged even after 2000 h heat resistance test regardless of the presence of the underlayer.

Other study (not published) shows that the AlN underlayer with only 6 nm thickness improve heat resistance.

![Fig. 4. Cross-sectional TEM image. (a): PI/AlN/(Al,Ti)N. (b): Interface between crystalline AlN underlayer and (Al,Ti)N.](image)

![Fig. 5. Cross-sectional TEM image. (a): PI/AlO$_x$/ (Al,Ti)N. (b): Interface between amorphous AlO$_x$ underlayer and (Al,Ti)N.](image)

![Fig. 6. Cross-sectional TEM image. (a): PI/SiN$_x$/ (Al,Ti)N. (b): Interface between amorphous SiN$_x$ underlayer and (Al,Ti)N.](image)

![Fig. 7. Change in electrical resistance $\Delta R_{25}$ after heat resistance tests at 260 °C in thermistor elements with and without crystalline AlN underlayer.](image)
The 50 nm underlayer in this study is enough to suppress the resistance change.

This demonstrates that the heat resistance of thermistor on resin film can be improved by inserting an underlayer of any crystallinity between the PI substrate and (Al,Ti)N thin film, as long as the resistivity of the underlayer is much higher than the thermistor. The formation of amorphous oxynitride can be suppressed by inserting underlayer, which prevent (Al,Ti)N taking oxygen from the PI substrate during the initial growth of (Al,Ti)N. These results support the assertion that the amorphous oxynitride layer that forms during initial growth of (Al,Ti)N significantly affects the degradation of heat resistance.

In this study, the degradation of resistance caused by the interface between the PI substrate and (Al,Ti)N has been almost completely solved. However, the degradation in resistance due to the thermistor material itself remains. We intend to fabricate higher heat resistance (Al,Ti)N thin films by optimizing the crystal growth conditions in future work.

In practice, AlOx and SiNx are difficult to process by wet etching and the mechanical strength is relatively low. Considering the mechanical properties and etching suitability, we selected modified AlN materials as candidates for the underlayer, and successfully developed a thermistor sensor that is both thin and heat resistant.

4. Conclusion

We analyzed the interface between the PI substrate and (Al,Ti)N thin film to understand the mechanisms of heat degradation in thin-film thermistors with wurtzite (Al,Ti)N nitride on resin films.

When (Al,Ti)N is deposited directly on PI substrate, an amorphous oxynitride layer forms during the initial growth of (Al,Ti)N. However, the amorphous oxynitride layer during initial growth disappeared by the insertion of an underlayer such as crystalline AlN or amorphous AlOx, SiNx, or SiOx between the PI substrate and (Al,Ti)N.

In addition, the thermistors with an underlayer exhibited similar tendencies in terms of the change in resistivity during heat resistance testing regardless of crystallinity and composition, and exhibited much superior properties to thermistors without an underlayer.

Observation of the interface between the underlayer and (Al,Ti)N layer revealed that columnar crystalline (Al,Ti)N grew without the formation of an amorphous layer during initial growth by sputtering. We therefore concluded that the inserted underlayer prevents (Al,Ti)N from taking oxygen from the PI substrate, which suppresses the formation of amorphous oxynitride and suppresses heat degradation at high temperatures.

The thin-film thermistor elements developed in this study are expected to contribute to the measurement of temperatures with high accuracy and to the long life of electronic devices with limited space in high-temperature environments.

Furthermore, we expect that this study will play an important role in design guidelines for functional ceramic thin films on resin substrates.

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