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Woodceramics Thin Films Grown by RF magnetron Sputtering

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Woodceramics (WCMs) thin films have been prepared by radio frequency (RF) magnetron sputtering. Electrical properties of WCMs thin films have been studied. Growth rate of WCMs thin films decreases with growth temperature and increases with RF input power. Growth temperature dependence of the electrical resistance for WCMs thin films has a maximum at growth temperature of 220°C. RF power dependence of the resistance decreases monotonically with RF power. The B constant as a thermistor for WCMs thin films was derived and about 6.7×10^2 K. Electrical resistance decreases by an amount of 92% as humidity changes from 20%RH to 80%RH. The amount is larger than that for bulk WCMs. Thus, it seems that the WCMs thin films are suitable for temperature and humidity sensors.

Key words : woodceramics, humidity sensor, thin films, electrical properties, radio frequency magnetron sputtering

1. INTRODUCTION

Woodceramics (WCMs hereafter) are new porous ceramic materials and have shown a strong promise of constituting the next generation of industrial materials. Over the past few years a considerable number of studies have been made on the application of WCMs to a variety of fields such as building materials, infrared heaters, electromagnetic shielding materials, temperature sensors, and humidity sensors [1-3]. The WCMs are fabricated by sintering woody materials impregnated with phenolic resin forming glassy carbon which reinforces a woody fiber structure. WCMs can be fabricated from wood waste, waste papers, sawdust, telephone books and so on. Accordingly, WCMs are drawing particularly strong attention as ecomaterials of low cost with the prominent characteristics of lightness, hardness, porosity, and corrosion and heat resistance. The WCMs contain sodium, calcium and magnesium etc. which are the constituent of wood by a small amount, so that WCMs are different from graphite, that is likely to have a new function.

Thus far, there appears to be surprisingly little work done on WCMs thin films. Kasai [4-6] reported that transmittance of WCMs thin films fabricated by radio frequency (RF) sputtering was larger than that for a-C films made from benzene and density and electrical resistance of WCMs thin films decreased as growth temperature increased. It is anticipated that new characteristics and applications can be found for WCMs thin films.

In this paper, WCMs thin films have been prepared by RF magnetron sputtering at various conditions. Humidity and temperature dependence of electrical resistance have been studied aiming at the usage of humidity and temperature sensors.

2. EXPERIMENTAL

The growth condition of RF magnetron sputtering is presented in Table 1. Medium density fiber board (MDF hereafter) made from pinus radiata was used to manufacture WCMs target. The MDF was impregnated with phenolic resin using an ultrasonic impregnation system. After the impregnated MDF was dried at 135°C, it was sintered at 1200°C in a vacuum furnace to form WCMs target. Pyrex glasses were used as substrates. The effect of growth conditions, in particular, growth temperature (200 - 300°C) and RF power (150 - 200 W) were examined in detail. Aluminum electrodes were evaporated in vacuum on the WCMs thin films to make ohmic contacts for measuring electrical resistance. The space between the

Table.1 Growth Condition

Target	Woodceramics (Sintered at 1200°C)
Target diameter	75 mm
Inret Gas	Ar
Pressure	5×10^{-2} Torr
Substarate	Pyrex Glass
Gas Flow Rate	15 cc / min
Growth Temperature	200 - 300°C
RF Power	150 - 200W
Distance between Target and Substrate	50 mm

Table 1 Chemical composition of bulk WCMs.

Composition	C	NaO	MgO	Al_2O_3	P_2O_5	SO_3	Cl	K_2O	CaO
Atomic Weight (%)	97.44	1.21	0.08	0.04	0.09	0.08	0.05	0.61	0.40

Table 2 Chemical composition of the WCMs thin film deposited at 200°C.

Composition	C	NaO	MgO	Al_2O_3	P_2O_5	SO_3	Cl	K_2O	CaO
Atomic Weight (%)	92.17	2.69	0.63	0.55	0.03	0.11	0.03	0.33	3.46

electrode was 2.8 mm. Temperature dependence of the electrical resistance was measured in vacuum below 1 x 10^{-5} Torr (1.33 x 10^{-2} Pa). Humidity dependence of the electrical resistance was measured in the chamber where humidity was controlled by suppling wet and dry nitrogen. Thickness of WCMs thin films was measured by surface profiler (DEKTAK : Vecco Instrum. Inc.). The structure and surface morphology were observed by the X-ray diffraction and scanning electron microscope techniques.

3. RESULT AND DISCUSSIONS

3.1. Chemical composition of the WCMs thin films

Chemical composition of the WCMs bulk target sintered at 1200°C was examined by x-ray fluorescence analysis, which is shown at Table 1. Table 2 represents the composition of the WCMs thin films deposited on glass substrate, where SiO_2 is eliminated from the data as the composition of glass substrate. The chemical composition of WCMs thin films is almost the same as the bulk, although the amount of the atomic weight differs a little.

3.2. Growth temperature dependence of growth rate and electrical resistance

Growth temperature dependence of the growth rate and electrical resistance for WCMs thin films is shown in Fig.1. Growth rate decreases monotonically with the growth temperature. The WCMs thin films are re-evaporated from the surface at the temperature range. The electrical resistance of the films is of the order of MΩ which is much larger than that of the WCMs target of order a few Ω. Electrical resistance indicates a maximum at 220°C. All of the WCMs thin films fabricated in this experiment show a flat structureless X-ray diffraction spectra. The absence of X-ray peaks is characteristic of amorphous structure of the films. Thus, the change of resistance on growth temperature is not caused by the change of structure but by the following reasons; (1) WCMs thin films are an a-C:H:O films where molecules with sp^2 and sp^3 bonding coexist [6]: it is likely that the ratio of two types of bonding has a influence on the change of resistance, and (2) a little change in the amount of the impurity elements during the evaporation of WCMs.

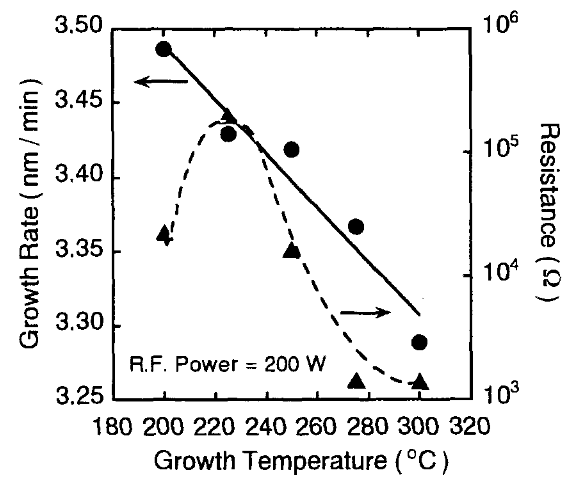

Fig.1 Growth temperature dependence of the growth rate and electrical resistance for WCMs thin films.

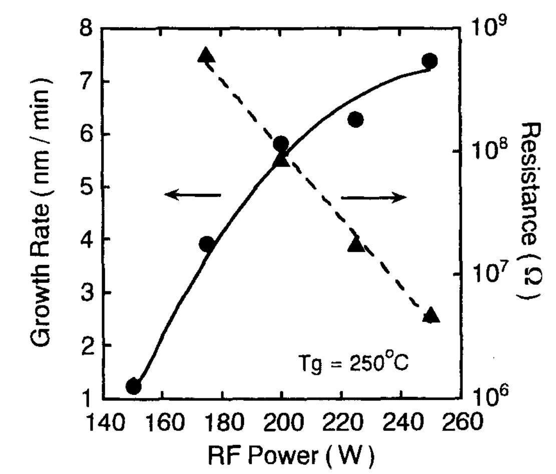

Fig.2 RF power dependence of the growth rate and electrical resistance for WCMs thin films.

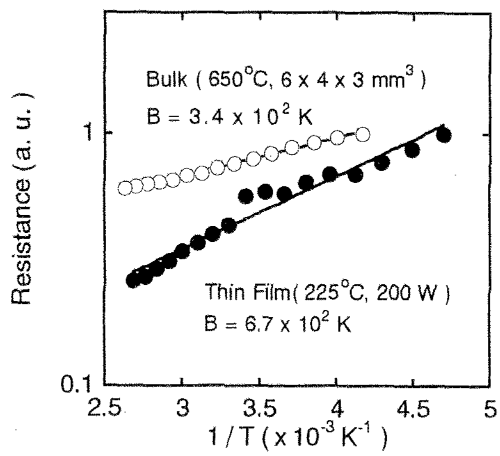

Fig.3 Temperature dependence of electrical resistance for WCMs thin fillm and bulk WCMs.

3.3. RF power dependence of growth rate and electrical resistance

Figure 2 shows the RF power dependence of the growth rate and electrical resistance. Growth rate increases and electrical resistance decreases monotonically with the RF power. A reason for the change of resistance might be attributed to the same reasons described in 3.2, although the details are not well understood.

3.4. Temperature dependence of electrical resistance

Arrhenius plots of the electrical resistance are presented in Fig.3 for the WCMs thin films grown at 225°C and input power of 200 W together with the bulk WCMs sintered at 650°C. The data is normalized for the comparison. Both electrical resistances decrease with increasing temperature; indicating negative temperature coefficient like semiconductor. The B value as a thermistor is expressed by

$$B = \frac{\ln R_1 - \ln R_2}{1/T_1 - 1/T_2} \qquad (1)$$

where R_1 and R_2 are the electrical resistance at the absolute temperature T_1 and T_2, respectively. From Fig.3, the B value of WCMs thin films was derived as 6.7×10^2 K which is larger than that of bulk WCMs, 3.4×10^2 K.

In general, electronic conduction and ionic conduction exist simultaneously in porous ceramics [7]. At low humidity, electronic conduction plays a major role, while ionic conduction plays a major role at high humidity. It was reported that there existed much difference on the temperature dependence of resistance for bulk WCMs between vacuum and air at humidity of 10%RH [8]. On the other hand, the temperature dependence of resistance for WCMs thin films presented almost the same tendency in vacuum

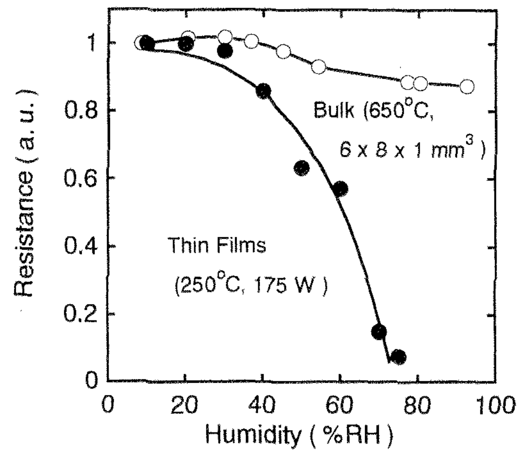

Fig.4 Relative humidity dependence of the electrical resistance for WCMs thin fillms and bulk WCMs.

and in air. Thus, electronic conduction is dominated than ionic conduction in the case of WCMs thin films.

3.5 Humidity dependence of electrical resistance

Humidity dependence of the electrical resistance is presented in Fig.4 for WCMs thin films grown at 250°C and RF power of 175 W. As the humidity increases from 20%RH to 80%RH, the decreasing rate of electrical resistance for WCMs thin films indicates 95% decrease which is much larger than that for bulk WCMs. The change of electrical resistance for bulk WCMs on humidity is caused by the adsorption of water molecules at the porous WCMs surface, yielding H_3O^+ and OH^- ions. Figure 5 shows the surface morphology of WCMs thin films. The surface is smooth and the porous structure can not be observed. Therefore, the absorption of water

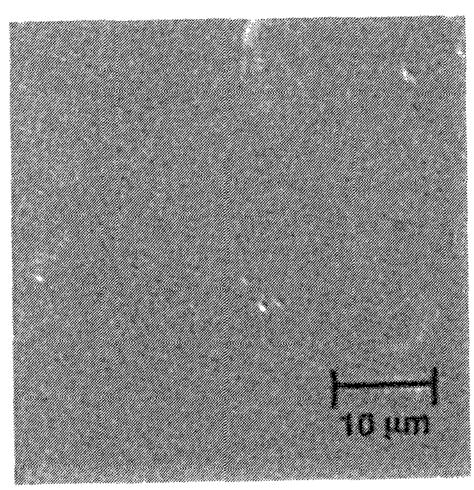

Fig.5 Surface morphology of WCMs thin film (rf power = 175W Tg = 250°C).

molecules at the surface and/or the stress of thin films may be taken into consideration for the resistance change in WCMs thin films upon the humidity changes.

4. CONCLUSION

The WCMs thin films of the ecomaterial have been prepared by RF magnetron sputtering at various conditions to study electrical properties. Growth rate of WCMs thin films decreases with growth temperature and increases with RF power. Electrical resistance of WCMs thin films has a maximum at growth temperature of 220°C; it decreases monotonically as RF power increases. The B constant as thermistor for WCMs thin films was about 6.7×10^2 K and the resistance changed by 95% as the humidity changed from 20%RH to 80%RH, which was much larger than that for bulk WCMs. The electrical resistance of the films was of in the order of MΩ. Consequently, it seems that the WCMs thin films are suitable for temperature and humidity sensors.

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