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Properties of magnetron-sputtered electrically insulating Al_2O_3 coatings on copper

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Amorphous Al_2O_3 coatings were deposited on Cu substrates with metallic bond layers by different magnetron-sputtering processes. Such sputtering conditions as the type of discharge, target material, total pressure, sputtering gas composition and substrate temperature were varied to study the process effects on the structure and properties of the coatings deposited. The structure and general properties were found to be strongly dependent on the type of process and parameters. The breakdown voltages did not show any significant lowering as the temperature was increased from 20 to 400–500 °C. The maximum temperature without formation of cracks in the Al_2O_3 coating on Cu was about 700 °C. The d.c. electrical conductivities of the Al_2O_3 were similar to that of bulk Al_2O_3 at different temperatures. The results reveal the potential use of magnetron-sputtered Al_2O_3 coatings on Cu for electrical insulation and oxidation protection in different high-temperature applications, e.g. on metallic magnetohydrodynamic electrode and insulator modules.

1. Introduction

Alumina (Al_2O_3) is an important material frequently used for various applications in which good electrical insulating properties are required at low and at high temperatures [1]. Thin coatings of Al_2O_3 have been synthesized by a variety of sputtering processes, including radio frequency (r.f.) diode-sputtering [2–11], reactive diode-sputtering with r.f. or direct current (d.c.) discharge [12, 13], r.f. magnetron-sputtering [14–16] and by reactive r.f. or d.c. magnetron-sputtering [17–19]. Such films have mainly been evaluated for applications in microelectronics [2, 4, 6, 15] and for wear- and corrosion-resistant coatings [16, 19]. Al_2O_3 coatings have also been prepared for high-temperature electrical insulating films in thin-film thermometers and fluxmeters [20–24].

Sputtered Al_2O_3 coatings can also be considered as potential electrically insulating coatings on Cu electrode and insulator modules in channels of a magnetohydrodynamic (MHD) generator, as proposed recently [25–27]. Requirements for such coatings are a good adhesion to the Cu substrate, a good thermal stability at the working temperature of 400–500 °C of the Cu modules, a dense microstructure and good electrical insulating properties during long-time operation at such high temperatures. The typical interelectrode voltage to be insulated in the MHD flow channel varies between 30 and 70 V. A coating thickness of 5–10 μm is expected to be adequate in this application [27].

In our previous works we have studied the structure and insulating properties of r.f. diode-sputtered Al_2O_3 [7] and MgO [28] coatings, but the deposition rates of the diode-sputtering processes usually stay very low for compounds such as Al_2O_3 and MgO. However, the deposition rates can be increased by using magnetron cathodes instead of conventional diode cathodes.

The aim of this work was to study the preparation, structure and electrical insulating properties of Al_2O_3 coatings prepared by different planar magnetron-sputtering techniques on Cu substrates. To our knowledge, data on electrical insulating properties such as the breakdown voltage and d.c. conductivity from room temperature to 600 °C and above are not readily available in the literature. Mainly the room-temperature properties of magnetron-sputtered Al_2O_3 have been reported [15].

2. Experimental procedure

2.1. Substrate material

The substrate material used in this study was oxygen-free high-conductivity copper (OFHC-Cu, Outokumpu Poricopper Oy). Copper discs had a diameter of 8–40 mm and a height of 5 mm, depending on the type of test and investigation. The substrates were first ground with emery paper and then polished with velvet cloth in an alumina/water suspension to obtain a mirror-like surface.

2.2. Coating procedures

The coatings were prepared in a laboratory-scale magnetron-sputtering unit by non-reactive and reactive magnetron-sputtering processes. The Al_2O_3 layers were deposited non-reactively by r.f. magnetron-sputtering from a compound target (purity of Al_2O_3,

0022-2461

99.99%) or reactively by r.f. or d.c. magnetron-sputtering from a metal target (purity of Al, 99.5%). In reactive sputtering the metal target was in the oxidized state (poisoned target).

The sputtering unit used consisted of a vacuum chamber with a diameter of 700 mm and a height of 270 mm, heatable substrate tables, a manipulator to move the substrate pallet from one substrate table to another, two planar magnetron cathodes with a target diameter of 150 mm, a shutter, mass-flow controllers for argon and a reactive gas, a total pressure controller equipped with a capacitance manometer, a cryopumping system (pumping speed for argon $1200\,\mathrm{l\,s^{-1}}$), an 800 W r.f. power supply (13.56 MHz), a 5 kW current-controlled d.c. magnetron power supply and a d.c. bias/etch power supply with a maximum voltage of -700 V.

The Cu substrates were ultrasonically cleaned in acetone and put on the substrate pallet, which was transferred into the sputtering chamber through a pre-vacuum chamber. First the samples were heated and sputter etched with a potential of -700 V for 10 min at a pressure of 3.33 Pa. This was followed by the d.c. magnetron bias sputtering of a metallic Ti or Cr bond layer with a thickness between 1 and 2 μm. The sputtering pressure and substrate temperature were 0.67 Pa and 500 °C, respectively. When the Al_2O_3 layer was reactively sputtered from a metallic target, a bond layer of sputtered Al was used. Some Al_2O_3 coatings were sputtered directly on Cu substrates without any bond layer, but this always led to poor bonding of the Al_2O_3 layer to Cu. Such coatings could not be exposed to elevated temperatures without debonding from the substrate. In addition to improving the adhesion of Al_2O_3 films to Cu, the sputtered metallic bond layers served also as barrier layers preventing diffusion of Cu into the film during sputtering, as recently described for sputtered MgO coatings on copper [29].

The main sputtering parameters for the deposition of Al_2O_3 coatings with some of the properties of the coatings are shown in Table I.

2.3. Structural studies

The structural studies were carried out with a Philips SEM 515 scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS) microanalyser and by Siemens Diffrac 500 X-ray diffractometer (XRD) using $\mathrm{Cu}K_\alpha$ radiation. The coating thickness was measured from the SEM micrographs and by the ball cratering method. The film density was determined from the weight gain and the thickness of the Al_2O_3 coating. The weight of the Cu substrate with a bond layer was previously measured.

2.4. Thermal cycling and annealing studies

Sputter-deposited samples with a diameter of 15 mm and a height of 5 mm were thermally cycled 100 times between room temperature and 600 °C in air. The tests were carried out by automatically transferring the samples in a quartz tube with one end shut into and out of a laboratory furnace. The average heating and cooling rates of the samples were 150 and $100\,^\circ\mathrm{C\,min^{-1}}$, respectively. The samples were evaluated by an optical stereo microscope after 1, 10, 50 and 100 cycles. After finishing the test the samples were evaluated by SEM and EDS. Additional information was obtained from the electrical measurements, in which the samples were heated from room temperature to a maximum temperature of 600–900 °C.

2.5. Electrical insulation measurements

The electrical insulation properties of the coatings were evaluated by electrical breakdown voltage measurements and by d.c. conduction measurements at different temperatures. The breakdown voltage measurements were performed at room temperature and at elevated temperatures up to the temperature range 600–900 °C in air and in an argon atmosphere. The testing apparatus had a grounded sample holder and a hemispherical Cu top electrode with a radius of 5 mm. The top electrode was in contact with the coated surface with a weight of 0.33 kg(f). The high-voltage power supply had a maximum voltage of 5 kV and a maximum current of 20 mA. The voltage across the insulating coating was recorded with an X–Y plotter (voltage versus time) and the leaking current was monitored as a voltage drop across a resistor. A positive d.c. voltage was raised manually at a rate of approximately $150\,\mathrm{V\,s^{-1}}$ until a sharp increase in the current and a decrease in the voltage due to breakdown was observed. The equipment allowed the repositioning of the electrode for further measurements. At least five breakdown measurements were carried out at each temperature.

A fully protected three-electrode system was used to measure the d.c. conductivity of Al_2O_3 coatings as a function of temperature in an argon atmosphere. Argon was selected as an atmosphere to prevent oxidation-related effects, e.g. oxidation of the substrate, of the grounded ring-type shield electrode and of the measuring electrode made of Cu. The samples had sputtered gold layers on the surface of the Al_2O_3 coating to give a good electrical contact and a well-defined measuring area. The diameter of the sputtered contact electrode was 7 mm (area $38.5\,\mathrm{mm^2}$). A polished flat copper disc with a diameter of 7 mm and height 2 mm was put on the gold contact and a copper rod was in contact with the disc. A voltage-stabilized d.c. power supply was used to apply a positive voltage of 1–50 V to the substrate. The ring-type electrode was used to eliminate the surface conduction. The leaking current through the coating was measured with a Keithley 614 electrometer 1 min after applying the voltage. Currents as low as 0.05 pA could be measured reliably. The conductivity values presented here were measured with a voltage of 20 V, which corresponds to an electric field of $10^4\,\mathrm{V\,cm^{-1}}$ for a coating 20 μm thick. In some cases no sputtered gold contacts were used due to problems in obtaining high resistance between the gold contact electrode and the

TABLE I Process parameters and properties of magnetron-sputtered Al_2O_3 coatings

Run[a]	Target	Gas flows		Oxygen in gas	Substrate temperature	Deposition pressure	Target voltage	Substrate voltage[b]	Distance (mm)	Deposition time	Coating thickness	Growth rate	Stoichiometry[c] O:Al	Argon content[c]
		Ar	O_2 (ml min^{-1})	(%)	(°C)	(Pa)	(V)	(V)		(h)	(μm)	(μm h^{-1})		(at %)
C24	Al_2O_3	50	0	0	< 200	1.06	− 465	f/	45	5	8	1.6	1.35	0.47
C26	Al_2O_3	50	0	0	450	0.40	− 440	f/	45	5	8	1.6		
C20	Al_2O_3	50	0	0	450	1.06	− 500	f/	45	5	15	3.0	1.42	0.25
C28	Al_2O_3	50	0	0	450	1.06	− 475	f/	45	1	3	3.0		
C31	Al_2O_3	50	0	0	450	1.06	− 480	g/0	45	5	9	1.8		
C07	Al_2O_3	50	0	0	450	2.00	− 520	f/	45	5	23	4.6		
C03	Al_2O_3	99	1	1	450	1.06	− 490	f/	45	5	3	0.6	1.48	0.14
C02	Al_2O_3	47.5	2.5	5	450	1.06	− 480	f/ + 17	45	5	2	0.4	1.51	0.14
C27	Al_2O_3	40	10[d]	20[d]	< 200	1.06	− 460	f/ + 10	45	5	4	0.8	1.47[e]	0.60
M09	Al	20	10	33	< 200	1.06	− 140	f/	65	5	0.6	0.1	1.80	0.20
M10	Al	20	10	33	500	1.06	− 140	f/ + 3	65	20	3.8	0.2	1.80	0.21
M08	Al	20	20	50	< 200	0.40	− 285	f/ − 30	65	3	2.5	0.8	1.90	0.26

Target power 600 W r.f., except in M08 1140 W d.c.
Power density 3.4 W cm^{-2}, except in M08 6.3 W cm^{-2}.

[a] C, compound target; M, metal target.

[b] f, Floating potential; g, grounded potential.

[c] Stoichiometry and argon content by RBS [30].

[d] Reactive gas, N_2.

[e] Stoichiometry, (O + N) : Al.

substrate. This was the case especially with thin Al_2O_3 coatings with some local defects.

3. Results and discussion

3.1. Structure of the Al_2O_3 coatings

The growth rate of Al_2O_3 coatings was found to be affected by such sputtering parameters as the total pressure, gas composition and substrate temperature, as shown in Table I. Typical growth rates of Al_2O_3 coatings prepared on heated substrates by r.f. magnetron-sputtering from the compound target were $1.6\ \mu m\ h^{-1}$ at 0.40 Pa, $3.0\ \mu m\ h^{-1}$ at 1.06 Pa and $4.6\ \mu m\ h^{-1}$ at 2.00 Pa. This kind of behaviour can be explained by the increase of ionization with pressure, as stated elsewhere [2]. The increase in growth rate with increase in pressure was also associated with a growth of a less dense microstructure, as is well illustrated in Fig. 1. Apparently the increase in scatter of the sputtered atoms from the gas atoms results in a typical growth of coatings with a lower density. The substrates were also at a floating potential, which was detected to be typically between +10 and +20 V. Evidently, such a positive potential prevents all possible film bombardment by positive plasma ions, which could improve the microstructure. This is probably not the case when sputtering was done on grounded substrates, where a potential drop from a positive plasma to the surface of the grounded substrate can cause low-energy ion bombardment at the substrate. Indeed, such coatings had a somewhat denser microstructure, as shown in Fig. 2. Such coatings had a typical growth rate of $1.8\ \mu m\ h^{-1}$, which is less than that of the corresponding coatings sputtered on floating substrates.

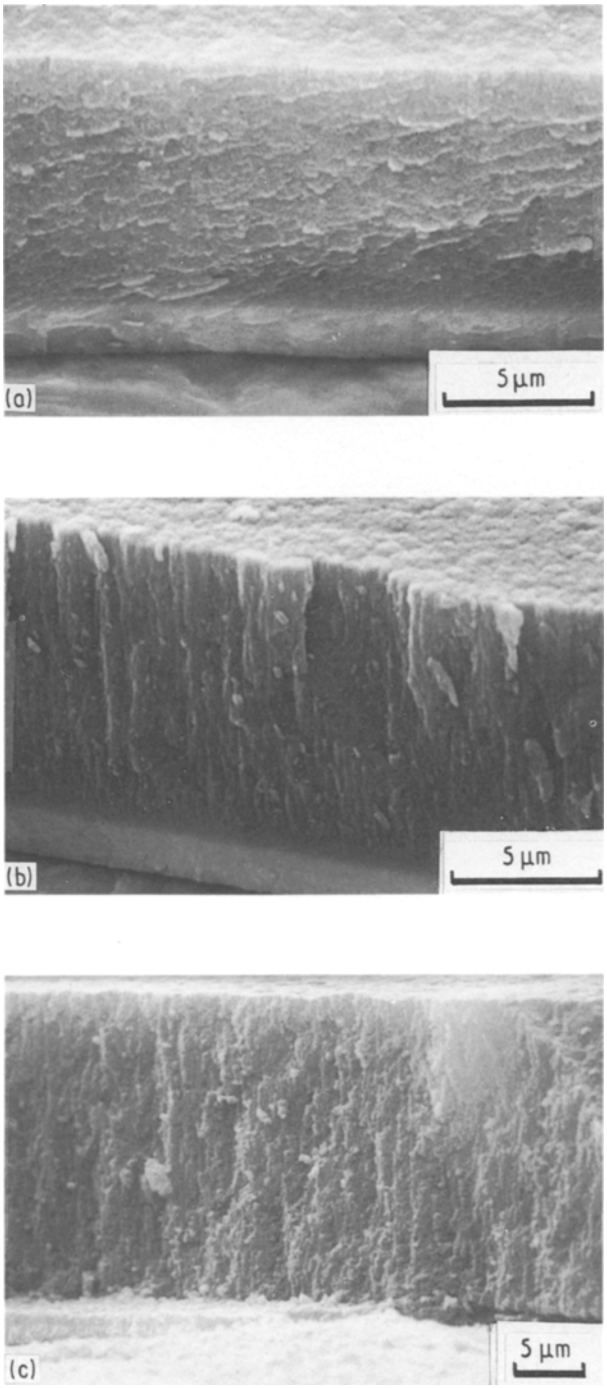

Figure 1 Effect of total pressure on the microstructure of Al_2O_3 coatings prepared by non-reactive r.f. magnetron-sputtering from the compound target on heated Cu substrates. Pressure: (a) 0.40 Pa (run C26), (b) 1.06 Pa (run C20) and (c) 2.00 Pa (run C07). For other parameters, see Table I.

When the deposition was done on unheated floating substrates the growth rate was somewhat lower, typically $1.6\ \mu m\ h^{-1}$, than when sputtering on heated substrates. These coatings were relatively dense in their microstructure, but they were black in colour and strongly substoichiometric, as shown in Fig. 3 and Table I. Such coatings had a smooth and a more glass-like fracture surface than films sputtered on heated substrates. It should be mentioned here that, at least in principle, heating of the substrates was needed to ensure a good adhesion, a dense microstructure and a low argon content.

The use of small amounts of oxygen (1 or 5%) led to a pronounced decrease in the growth rate: $0.4\ \mu m\ h^{-1}$ for 5% O_2 and $0.6\ \mu m\ h^{-1}$ for 1% O_2. These findings are mainly consistent with those reported for r.f. diode-sputtered Al_2O_3 coatings by Chen and co-workers [9, 10] and for r.f. magnetron-sputtered films by Nowicki [15]. In our films the decrease in the growth rate was much greater than the one-half reported by Nowicki [15].

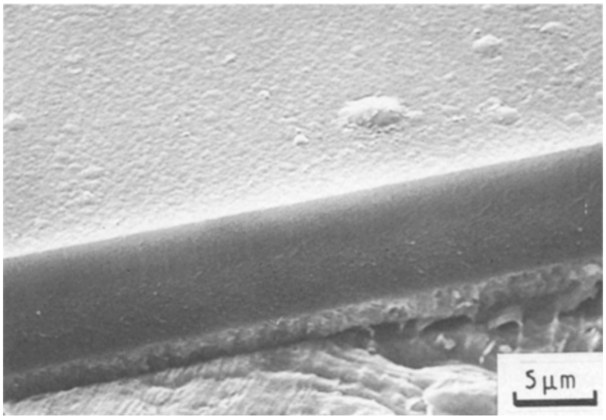

Figure 2 Microstructure of an Al_2O_3 coating prepared by non-reactive r.f. magnetron-sputtering from the compound target on a grounded substrate. Pressure 1.06 Pa, temperature 450 °C and Cr bond layer. For other parameters, see run C31 in Table I.

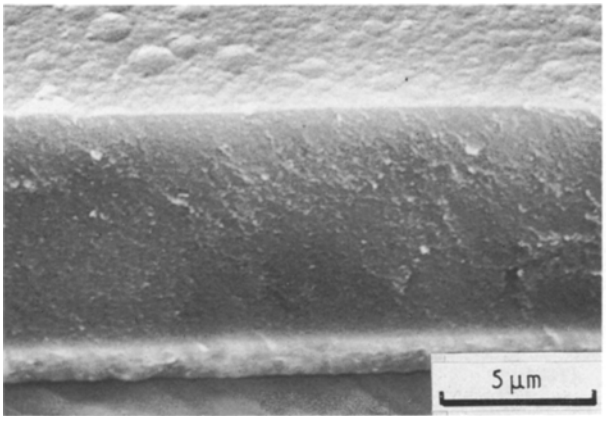

Figure 3 Microstructure of an Al_2O_3 coating prepared by non-reactive r.f. magnetron-sputtering from the compound target on an unheated substrate. Pressure 1.06 Pa, gas Ar and Cr bond layer. For other parameters, see run C24 in Table I.

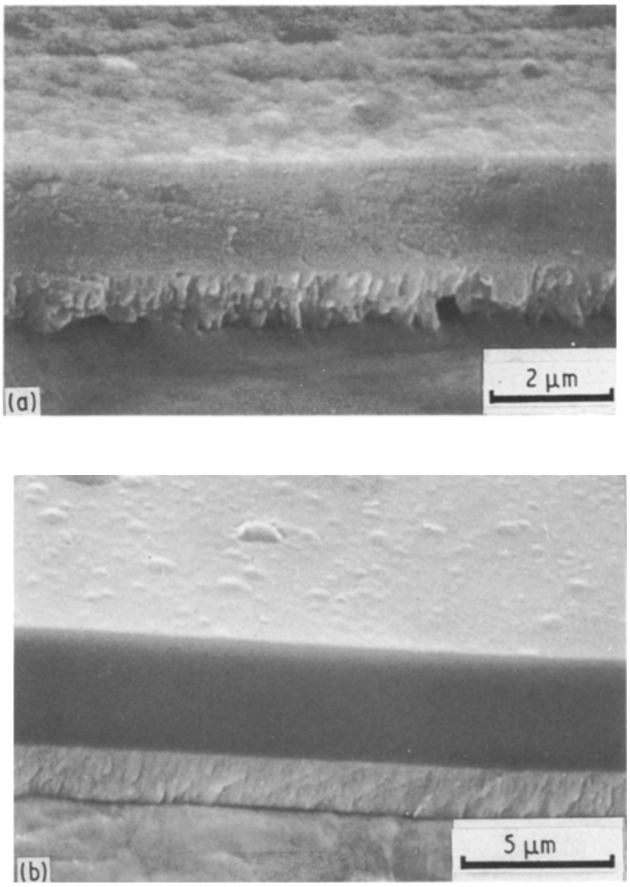

Figure 4 Microstructure of Al_2O_3 coatings prepared by r.f. magnetron-sputtering from the compound target in a gas mixture of (a) Ar + 5% O_2 (run C02) and (b) Ar + 20% N_2 (run C27). Substrate temperature and bond layer: (a) 450 °C, Ti and (b) < 200 °C, Cr. For other parameters, see Table I.

Most of the coatings in this work were sputtered in pure argon in order to avoid unreasonably long sputtering times. As is discussed below, such coatings showed sufficiently good insulation characteristics for the present purpose. However, it is evident that sputtering with small amounts of oxygen yielded transparent and highly stoichiometric coatings, whereas coatings sputtered in pure argon were slightly substoichiometric and yellowish or brownish in colour, as described in [30]. Also, nitrogen could be used to compensate the oxygen deficiency, but the growth rate was again only about 0.8 $\mu m\ h^{-1}$. Fig. 4 illustrates the microstructure of two r.f. magnetron-sputtered coatings, which were prepared from an Al_2O_3 target by using either oxygen or nitrogen in the sputtering gas mixture.

An experiment was carried out to determine the density of an Al_2O_3 coating prepared by r.f. magnetron-sputtering from the compound target on unheated substrate (C24 parameters), since according to SEM studies (see Fig. 3) such a film had a relatively dense microstructure. The Al_2O_3 layer was sputtered on a Ti bond layer on a Cu sample, which was weighed before the deposition of Al_2O_3. By using the increase in weight and thickness of the film, an average density of 2.71 $g\ cm^{-3}$ with an experimental error of ± 4% could be measured. The densities of crystalline α-Al_2O_3 and γ-Al_2O_3 are 3.98 and 3.2 $g\ cm^{-3}$, respectively [31]. Thus, the density of the amorphous Al_2O_3 film is lower than that of the crystalline phases. However, it agrees well with the density of 2.7 $g\ cm^{-3}$ determined for electron-beam evaporated Al_2O_3 films [32] and 2.97 $g\ cm^{-3}$ for r.f. magnetron-sputtered Al_2O_3 films [15].

Both d.c. and r.f. power supplies were used to sputter Al_2O_3 coatings using a metallic Al target in a gas mixture of argon and oxygen. Al_2O_3 coatings with oxide-like properties could be prepared only under conditions where the target was in the oxidized state (poisoned).

A series of d.c. sputtering runs was carried out to maximize the sputtering time, i.e. to get coatings thick enough by modifying the total pressure, oxygen partial pressure and target current. Under non-optimized conditions with a high total pressure and a high target current, severe arcing started after about 30 min sputtering, which resulted in the penetration of metallic microdroplets into the coating. Such inhomogeneities are undesirable in coatings to be used as electrical insulators. Run M08 in Table I represents a reactive d.c. magnetron-sputtering run, which could be extended up to 3 h sputtering without arcing.

Arcing was certainly not observed with the r.f.-powered metal target. The deposition rate of reactive r.f. magnetron-sputtering was unfortunately very low, being at maximum about 0.2 $\mu m\ h^{-1}$. Therefore, a relatively long sputtering time of 20 h was needed to deposit an Al_2O_3 coating with a thickness of about 4 µm. The reactive d.c. magnetron-sputtering gave somewhat higher growth rates of 0.8 $\mu m\ h^{-1}$ due to the higher target power level. Fig. 5 illustrates typical microstructures of reactively magnetron-sputtered Al_2O_3 films on Cu.

XRD studies revealed that all of the Al_2O_3 coatings prepared in this study were amorphous. No traces of crystalline phases of alumina could be detected even in spectra plotted with highly magnified *Y*-axis. The findings are in good agreement with those of others in the literature [14–16].

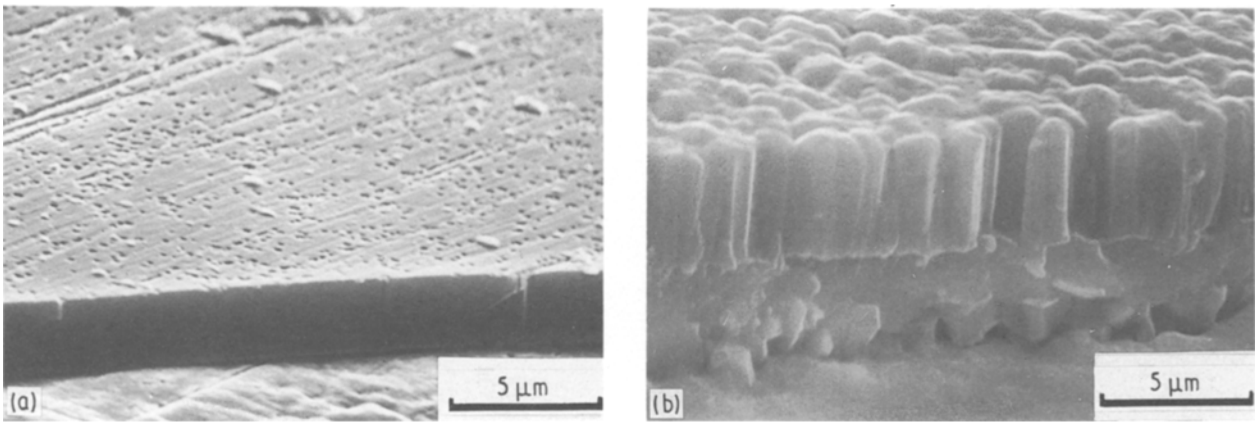

Figure 5 Microstructure of Al_2O_3 coatings prepared by reactive magnetron-sputtering processes from the metal target: (a) run M08 with d.c. power, gas Ar + 50% O_2, temperature < 200 °C and no bond layers; (b) run M10 with r.f. power, gas Ar + 33% O_2, temperature 500 °C and Al bond layer. For other parameters, see Table I.

3.2. Structure of the sputtered metallic bond layers

XRD analysis of the sputtered double layer structure showed that sputtered Cr bond layers had a crystalline structure of cubic α-Cr (Joint Committee on Powder Diffraction Standards (JCPDS) Card 6-0694). Sputtered Ti bond layers after the Al_2O_3 sputtering on heated samples had a preferentially [0001] oriented α-Ti with variable amounts of intermetallic compounds of Ti and Cu. Such intermetallic phases as Ti_3Cu_4 (JCPDS Card 18-0460) and $TiCu_4$ (JCPDS Card 20-0370) and sometimes traces of such phases as $CuTi_2$ (JCPDS Card 15-0717), $CuTi_3$ (JCPDS Card 25-1144) and Cu_3Ti (JCPDS Card 7-0107/0108) were observed. In order to study whether the formation of intermetallics takes place during the sputtering of Ti or only during the sputtering of the Al_2O_3 top layer on heated substrates, samples with only the sputtered Ti layer and corresponding samples subsequently annealed at 450 °C for 6 h in high vacuum (samples were on the heatable substrate holder in the process chamber) were studied with the XRD analysis. Under the present sputtering conditions peaks of the metallic Ti bond layer and Cu substrate could be detected. However, annealing caused the growth of the peaks of different intermetallic phases of Ti and Cu, which clearly revealed that such phases did form during the sputtering of the Al_2O_3.

The sputtered Al bond layer had a metallic Al structure when sputtered on unheated substrates and an intermetallic Al_4Cu_9 (JCPDS Card 2-1254) structure when sputtered on heated substrates.

3.3. Thermal cycling resistance of Al_2O_3 on Cu

Cu electrodes in MHD channels are subjected to temperature variations during operation. Since the magnitudes of the thermal expansion coefficients of Cu and Al_2O_3 are markedly different, the coated structure will be strained by thermal stresses, which could deteriorate the insulation properties of the Al_2O_3 layer. Tensile stresses are expected to be present in Al_2O_3 coatings on Cu during heating, since the coefficient of thermal expansion of Cu is markedly higher than that of Al_2O_3 (Cu 17×10^{-6} K^{-1} and Al_2O_3 8×10^{-6} K^{-1}). The maximum temperature of 600 °C was selected for the reason that it is well above the maximum operation temperature of MHD electrodes.

Several Al_2O_3-coated samples with or without bond layers were subjected to the test with a maximum of 100 thermal cycles to 600 °C under the following conclusions. The use of a metallic bond layer between Cu and Al_2O_3 was found to be necessary, because coatings without bond layers peeled off after the first thermal cycles. However, coatings with either sputtered Ti or Cr bond layer were free of cracks even after 100 cycles to 600 °C in air. Fig. 6 illustrates the surface of some Al_2O_3 coatings after 100 cycles. No clear microstructural changes (e.g. microcracks) could be found at the coated surface, whereas it could be observed that the uncoated area of the Cu samples were strongly oxidized. The only mechanism that was sometimes found to deteriorate the Al_2O_3 coating was the disappearance of the substrate through oxidation at the edges of the coated disc. The side area of the disc had a rough unpolished surface, and therefore the coating deposited on it was not of good quality, which resulted in out-diffusion and oxidation of Cu. X-ray analysis of thermally cycled specimen revealed no crystallization of Al_2O_3. Usually the peak of metallic Ti had disappeared in the spectrum and peaks only from the Cu substrate and from the intermetallic phases of Cu and Ti were present. The peak of metallic Cr remained unchanged in those samples with sputtered Cr bond layers.

Reactively r.f. or d.c. magnetron-sputtered Al_2O_3 coatings were also in good and unchanged state after 100 cycles if they had the sputtered Al bond layer. In some cases the grey colour of the underlying bond layer had changed to yellow, indicating a phase transformation from Cu_9Al_4 to Cu alloyed with Al. Without bond layers the Al_2O_3 coating started to buckle during the first cooling from 600 °C. This followed cracking of the coating and severe oxidation of the substrate material. Fig. 7 shows an example of the surface structure of a reactively magnetron-sputtered

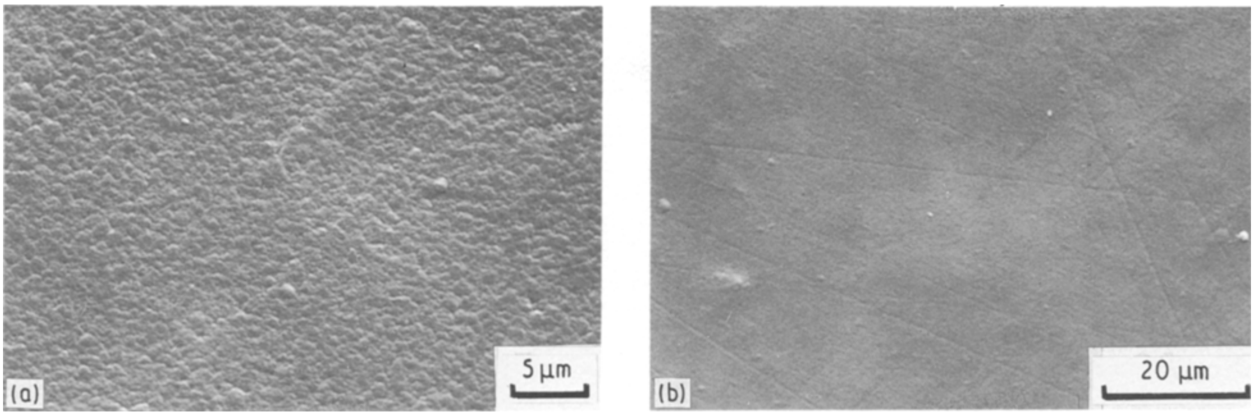

Figure 6 Surface views of two Al_2O_3 coatings on Cu substrates after 100 thermal cycles 600 °C in air. The coatings were prepared by non-reactive r.f. magnetron-sputtering. (a) Thickness of Al_2O_3 is 12 μm, Cr bond layer and parameters are those of run C20 in Table I; (b) thickness of Al_2O_3 is 3 μm, Ti bond layer and parameters were those of run C03 in Table I.

Al_2O_3 coating with a bond layer after 100 cycles to 600 °C.

Evaluation of the samples used in electrical measurements gave additional information about the effect of temperature on the stability of the coated structure. Samples heated to a maximum temperature of about 700 °C did not have detectable cracks, whereas samples heated to a temperature of 800 °C or above revealed a network of microcracks. Although such cracks could be very easily observed visually or by optical microscopy, by SEM such cracks could hardly be observed, as illustrated in Fig. 8. It is believed that the sputtered Al_2O_3 coating on Cu is prestressed in compression at room temperature, partially due to the thermal expansion mismatch of the coating and the substrate, and partially due to the growth stresses, which in the case of sputtered coatings are usually compressive. Therefore, upon heating the coating can remain without cracking up to a temperature at which the thermal tensile stresses exceed the tensile strength of the Al_2O_3 coating.

3.4. Breakdown voltage and dielectric strength properties

The breakdown voltage measurements were done in air or in a protective gas (argon). Since it was found that the atmosphere selected had a strong effect on the absolute breakdown values measured, most of the results given here were obtained from measurements done in argon.

Fig. 9 shows the effect of atmosphere on the temperature dependence of breakdown voltage. The corresponding breakdown field strengths are also given in the figure. Breakdowns in argon always started at lower voltages than those in air. The values measured with the experimental apparatus used showed a relatively large scatter, which is assumed to be due to the weak points in the coatings, the intrinsic breakdown mechanism and some thickness variation. Apparently, the lowest values at different temperatures represent the insulation characteristics of areas with local weak spots, e.g. the nodular-type defects shown in Fig. 10. The highest values measured represent the insulation properties of films free of local defects. All values between the highest and the lowest ones are assumed to be determined by the distance of the weak spot from the contact point of the high-voltage electrode and the Al_2O_3 coating.

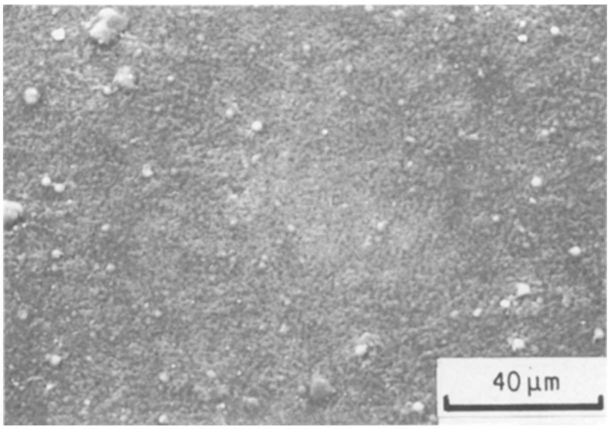

Figure 7 Surface view of a reactively r.f. magnetron-sputtered Al_2O_3 coating on Cu substrate after 100 thermal cycles to 600 °C in air. Thickness of Al_2O_3 is 3.8 μm, Al bond layer and parameters were those of run M10 in Table I.

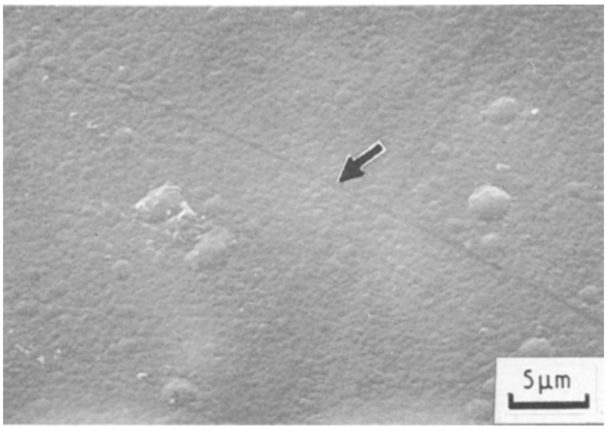

Figure 8 A crack formed in an r.f. magnetron-sputtered Al_2O_3 coating after heating in argon to 800 °C. The sputtering parameters of Al_2O_3 were those of run C31 in Table I.

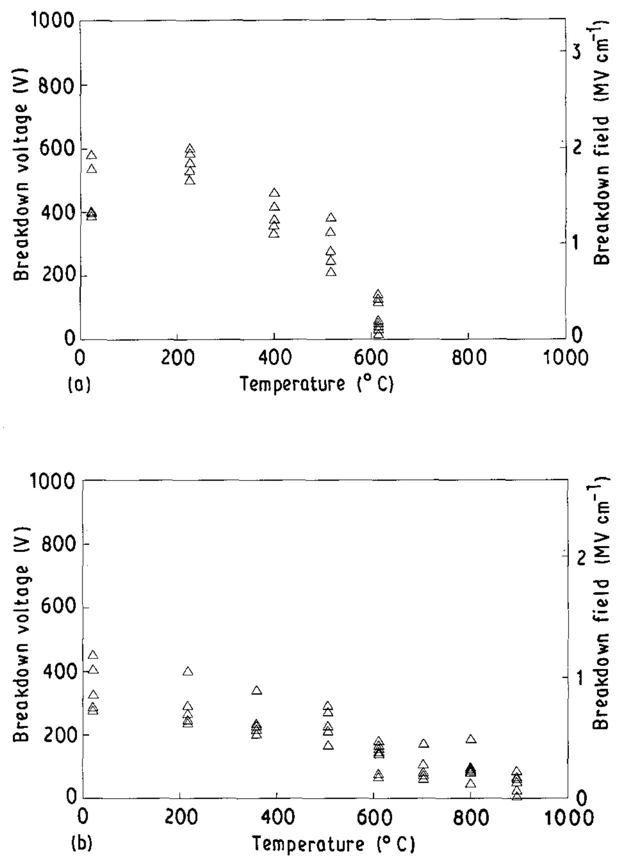

Figure 9 Electrical breakdown voltage and breakdown field of r.f. magnetron-sputtered $Al_2O_{3-x}N_Y$-type coatings as a function of temperature as measured (a) in air and (b) in argon. Sputtering parameters were those of run C27 in Table I and thickness (a) 3.0 μm and (b) 3.8 μm; Cr bond layer.

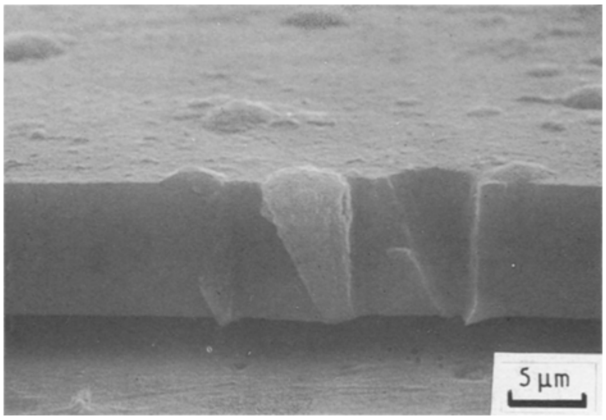

Figure 10 Al_2O_3 coating having nodular-type defects, which are assumed to be as weak spots for electrical insulation.

At lower measurement temperatures, i.e. at the region of the intrinsic breakdown mechanism, no leaking currents higher than the detection limit of 2 μA could be found. At higher temperatures a small leakage current of few hundred μA could be measured before the breakdown event. The transition temperature, above which such a current could be detected, was about 400–600 °C depending on the thickness of the Al_2O_3 coating. It was also noted that when the measurement was carried out at the temperatures at which the prebreakdown leakage currents were observed, the current showed a slow and continuing increase with time. It is obvious that a significantly lower rate of increase of the voltage would probably result in breakdowns at lower voltages than those measured with the rate of 150 V s^{-1} used in this study. Thus, the breakdown voltage values at very high temperatures can be regarded as rather optimistic.

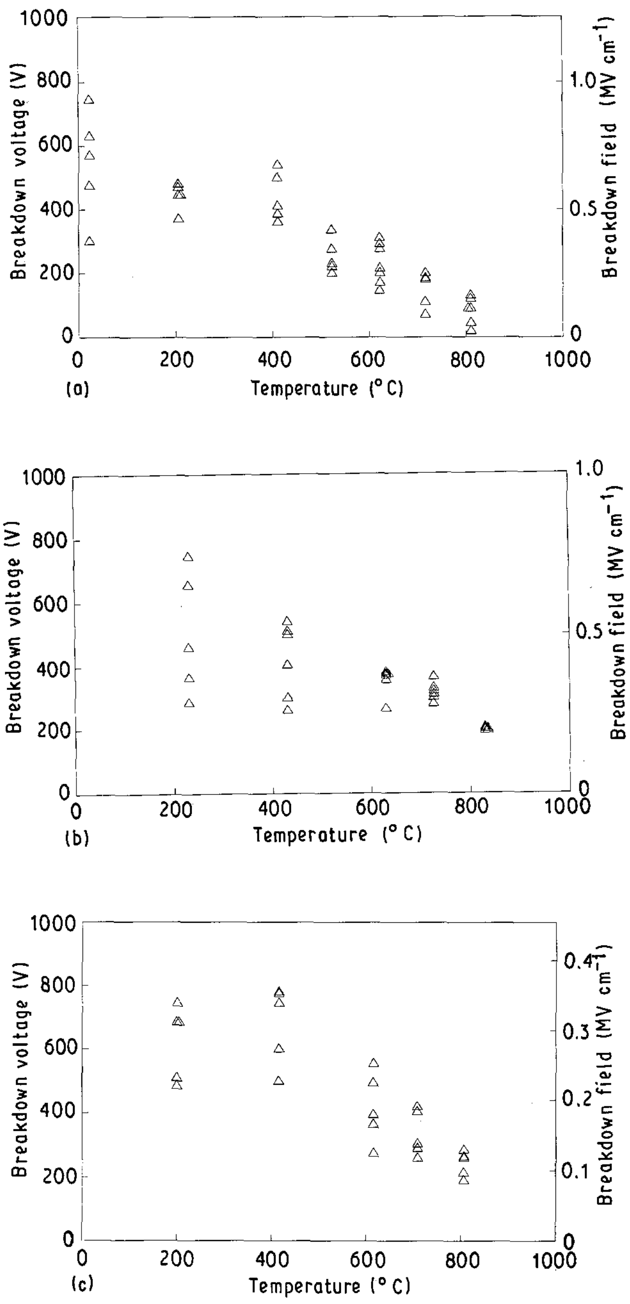

Figure 11 Electrical breakdown voltage and breakdown field strength of Al_2O_3 coatings as a function of temperature in argon. The coatings were prepared by non-reactive r.f. magnetron-sputtering at different total pressures on heated substrates kept at a floating potential. Sputtering pressure and thickness: (a) 0.40 Pa, 8 μm (run C26); (b) 1.06 Pa, 10 μm (run C20); and (c) 2.00 Pa, 22 μm (run C07).

Fig. 11 shows the results obtained with non-reactively r.f. magnetron-sputtered Al_2O_3 coatings, which were sputtered at different total pressures on heated and floating substrates. As presented above, the use of higher pressures also gives thicker coatings, and thus also resulted in higher absolute values of breakdown voltages. Fig. 12 shows the breakdown voltage properties of an Al_2O_3 coating non-reactively r.f. magnetron-sputtered on grounded substrates. In Fig. 9 the

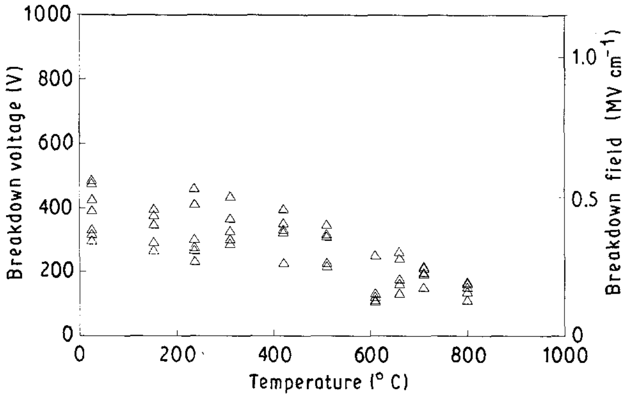

Figure 12 Temperature dependence of electrical breakdown voltage and breakdown field for an Al_2O_3 coating prepared by non-reactive r.f. magnetron-sputtering on a grounded substrate. Thickness of Al_2O_3 is 8.7 μm, substrate temperature 450 °C and parameters were those of run C31 in Table I.

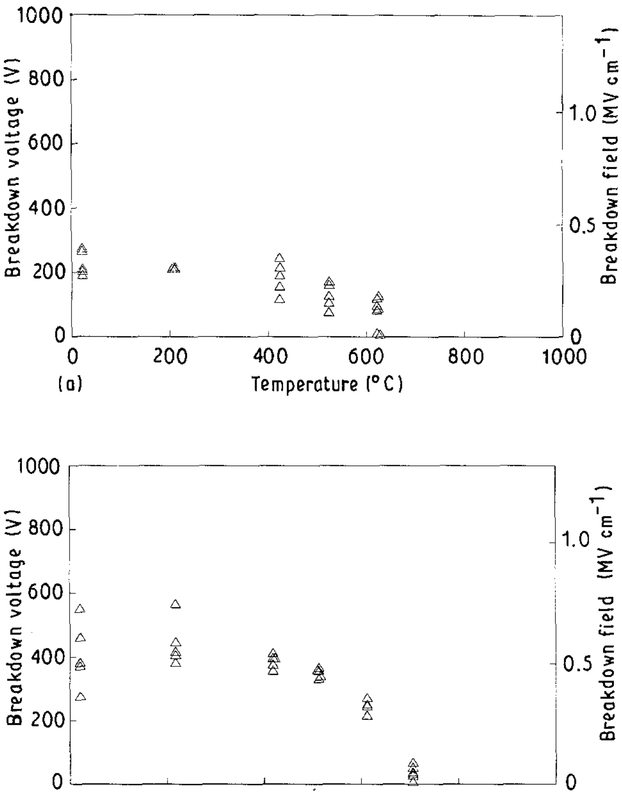

Figure 13 Temperature dependence of electrical breakdown voltage and breakdown field for non-reactively r.f. magnetron-sputtered and strongly oxygen-deficient Al_2O_3 coatings as measured (a) in argon and (b) in air. Parameters were those of run C24 in Table I, substrate temperature < 200 °C, gas was argon, Al_2O_3 target and thickness of Al_2O_3 is (a) 7.0 μm and (b) 7.6 μm.

$Al_2O_{3-x}N_y$-type coatings tested were prepared by r.f. magnetron-sputtering of the compound target in a gas mixture of Ar + 20% N_2.

The highest oxygen deficiency in the Al_2O_3 coatings (O/Al = 1.35) was observed in such coatings, which were prepared by non-reactive r.f. magnetron-sputtering from the compound target on unheated substrates. Such coatings, definitely due to the strong oxygen deficiency, showed measurable high leakage currents of the order of 0.6–0.9 mA well before the breakdown event in room temperature measurements. However, the films could insulate relatively high voltages even at high temperatures, as shown in Fig. 13. Annealing such coatings in air at 600 °C for 20 h eliminated the leakage conduction at the room-temperature measurements.

It has also been shown that the breakdown field (dielectric strength) has an inverse relationship to the sample thickness, i.e. the breakdown field strength decreases with the thickness [31]. This is also valid in results presented here, as shown, for example, in Fig. 14. The figure also illustrates the effect of oxygen content of the sputtering gas on the breakdown field at 200 °C in argon. It can be noted that the use of oxygen in r.f. magnetron-sputtering from a ceramic target did not give higher field values in films with similar thicknesses.

Fig. 15 shows the temperature dependence of breakdown voltage and field in two reactively magnetron-sputtered Al_2O_3 coatings as measured in argon. Relatively low absolute values were measured due to the low coating thickness. However, the coating prepared by reactive r.f. magnetron-sputtering preserves its insulation characteristics up to 600 °C and above.

The results given above showed clearly that the breakdown voltage remains relatively unchanged without marked lowering as the temperature is increased from room temperature to 400–500 °C, or above with the thickest coatings. This sort of behaviour is also well known in polycrystalline and single-crystalline bulk Al_2O_3 [31].

3.5. Electrical conductivity

The electrical conductivity of several Al_2O_3-coated samples was measured from room temperature up to 600 °C or above in an argon atmosphere.

Fig. 16 shows two typical curves of conductivity as a function of temperature for non-reactively r.f. magnetron-sputtered Al_2O_3 coatings on Cu. The curves were measured with the sputtered gold contacts. In Fig. 16a the conductivity of an Al_2O_3 coating with a thickness of 23 μm (film C07, Fig. 1c) was measured

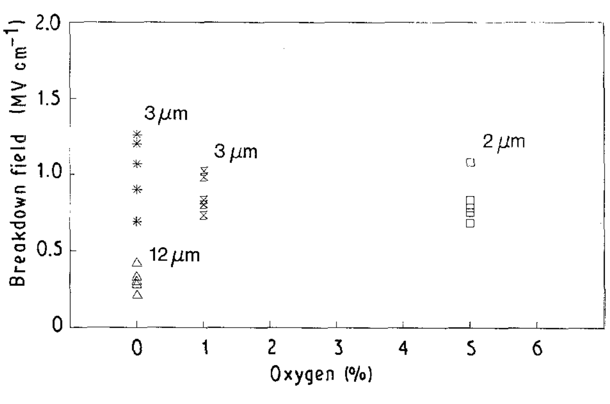

Figure 14 Measured breakdown field strengths of Al_2O_3 coatings, which were prepared by r.f. magnetron-sputtering with and without oxygen from the compound target on heated substrates. The thicknesses of the coatings are given in the figure. Measurement temperature 200 °C and test atmosphere argon.

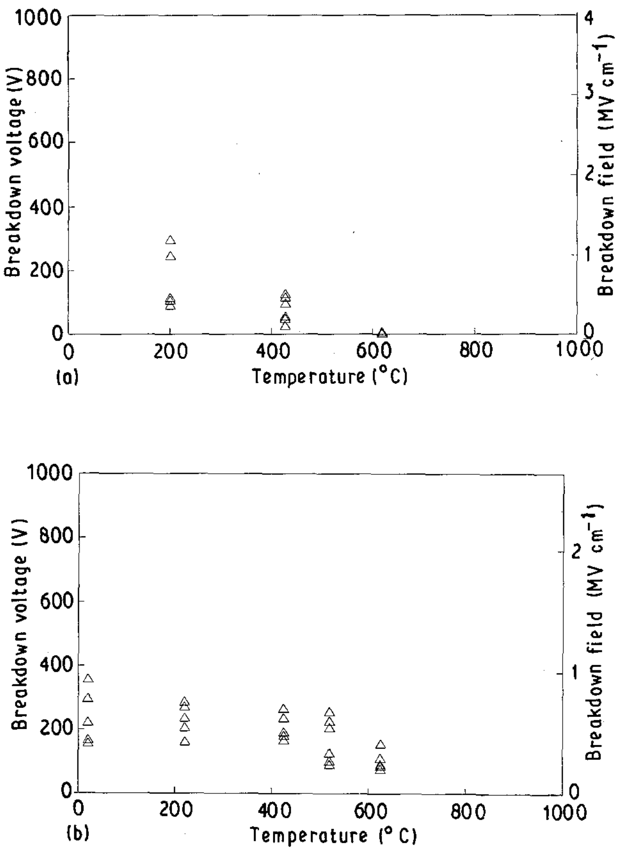

Figure 15 Temperature dependence of electrical breakdown voltage and breakdown field strength for reactively magnetron-sputtered Al_2O_3 coatings in argon: (a) reactively d.c. magnetron-sputtered Al_2O_3 coating with a thickness of 2.5 µm, parameters were those of run M08 in Table I; (b) reactively r.f. magnetron-sputtered Al_2O_3 coating with a thickness of 3.8 µm, parameters were those of run M10 in Table I.

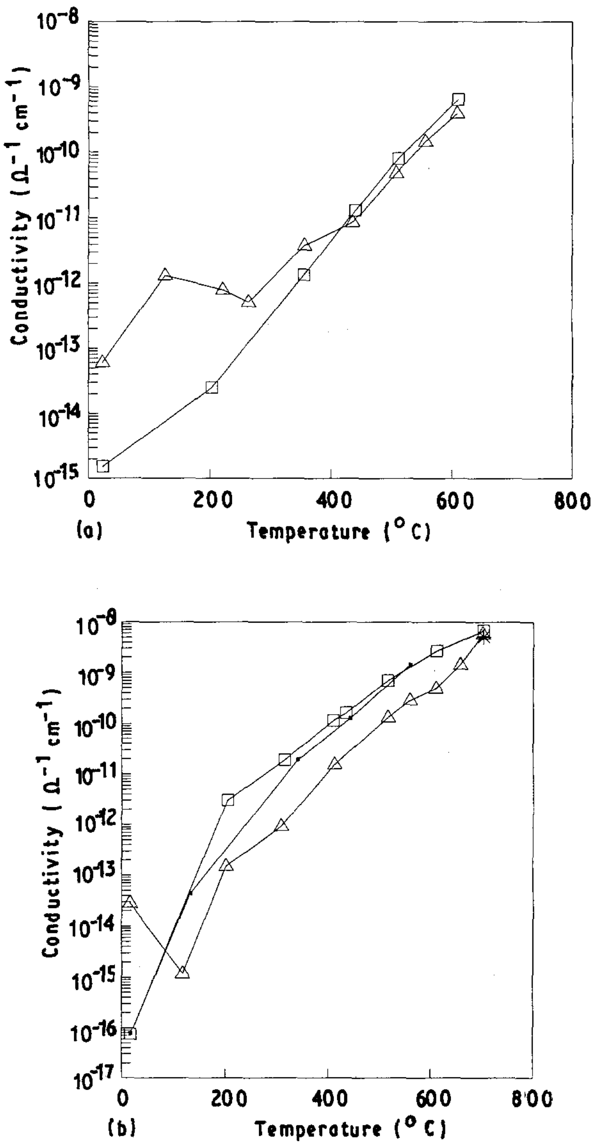

Figure 16 Electrical conductivity of Al_2O_3 coatings as a function of temperature. The coatings were prepared by non-reactive r.f. magnetron-sputtering from the compound target: (a) thickness of Al_2O_3 is 23 µm, Ti bond layer and parameters were those of run C07 in Table I; (b) thickness of Al_2O_3 is 15 µm, Ti bond layer and parameters were those of run C20 in Table I. (△) 1st heating, (●) 1st cooling, (□) 2nd heating and (*) 18 h at 700 °C.

during the first and second heatings to about 600 °C. During the first heating the conductivity remained relatively high at low temperatures. When further increasing the measurement temperature, lower conductivity values were measured. Such a behaviour is supposed to be caused by the evolution of moisture from the film, which results in a lower conductivity.

During the second heating no such behaviour was noted and low conductivities of the order of $1.5\times10^{-15}\,\Omega^{-1}\,cm^{-1}$ at room temperature could be measured. The conductivity values measured at 610 °C was $6.3\times10^{-10}\,\Omega^{-1}\,cm^{-1}$. The first heating curve for another Al_2O_3-coated sample in Fig. 16b shows a similar lowering of conductivity at low temperatures. During the first cooling and the second heating the conductivity showed somewhat higher values compared with the first heating except at the maximum temperature of 700 °C. Even after 18 h at 700 °C the same conductivity of about $5.0\times10^{-9}\,\Omega^{-1}\,cm^{-1}$ could be measured.

It should be mentioned that in some cases with other samples measured, the electrical insulation properties showed an abrupt collapse at high temperatures of the order of 600–700 °C, although satisfactory insulation characteristics below this temperature similar to those shown in Fig. 16 were measured. This can easily be explained to be effected by some local weak spots, in which, for example, the diffusion of the metallic species from the substrate, bond layers or measuring electrode can take place and thus short-circuit the electrodes. Fortunately, the temperature at which this was found to happen was well above the working temperature of 400–500 °C of Cu MHD electrodes.

Fig. 17 shows the electrical conductivity of an r.f. magnetron-sputtered Al_2O_3 coating prepared with similar parameters as the coating of Fig. 16b. In this case the measurement was carried out without the gold contact electrodes, which resulted in somewhat lower values compared with the use of the gold contacts. The conductivity of thin Al_2O_3 coatings (thickness 2–4 µm) could not be measured reliably with the gold contacts, because the resistance between the relatively large sputtered gold contact electrode and the substrate often showed a short-circuit or low resistance, indicating that there were some weak spots or inhomogeneities in the Al_2O_3 layer. Therefore, the

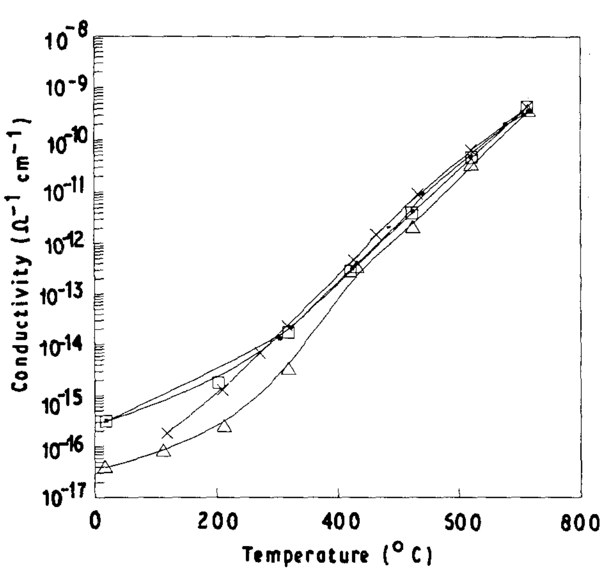

Figure 17 Electrical conductivity of Al_2O_3 coating against temperature. The coating was prepared by non-reactive r.f. magnetron-sputtering from the compound target. The measurement was carried out without the gold contacts. Thickness of Al_2O_3 is 11.5 μm, Ti bond layer and parameters were those of run C20 in Table I. Key as for Fig. 16.

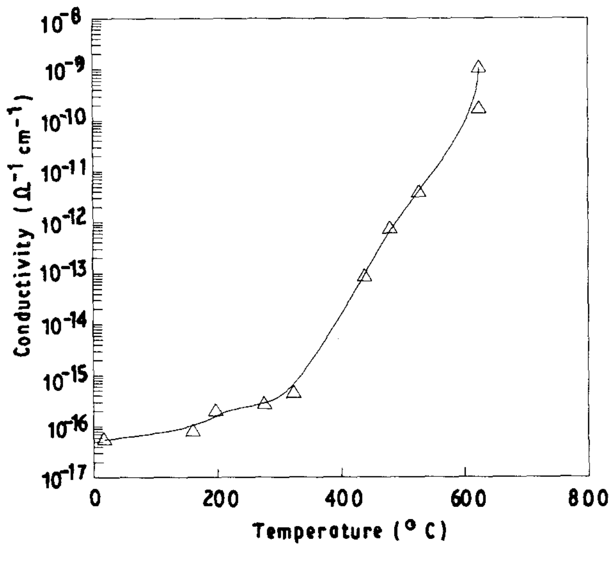

Figure 18 Electrical conductivity of Al_2O_3 coating against temperature. The coating was prepared by reactive r.f. magnetron-sputtering from the metal target. The measurement was carried out without the gold contacts. Thickness of Al_2O_3 is 3 μm, Al bond layer and parameters were those of run M10 in Table I.

conductivity was then measured without the gold contact electrodes. Fig. 18 presents a typical conductivity curve for a reactively r.f. magnetron-sputtered film with a thickness of 3 μm. The conductivity stays relatively low at low temperatures (partly due to poor contact by not using the gold contacts), but starts to increase at above 400 °C. Above 600 °C the film loses its insulation properties, probably due to the out-diffusion of Cu.

Generally, the values given here are in good agreement with conductivity values reported for bulk alumina [31]. Unfortunately, only a few published papers describe the conductivity in magnetron-sputtered Al_2O_3 and therefore comparison of the values is not possible. Nowicki [15] reported a conductivity value of $1 \times 10^{-12}\,\Omega^{-1}\,cm^{-1}$ at room temperature for r.f. planar magnetron-sputtered Al_2O_3, which is slightly higher than those presented in Fig. 16.

4. Conclusions

It has been shown that Al_2O_3 coatings can be deposited with metallic bond layers on Cu substrates by different magnetron-sputtering processes including non-reactive r.f. magnetron-sputtering, reactive r.f. magnetron-sputtering and reactive d.c. magnetron-sputtering.

Sputtered bond layers, such as Cr, Ti or Al, can be used to give the Al_2O_3 coating an adequate bonding against thermal cycling between room temperature and 600 °C in air. Cracks caused by the thermal expansion mismatch of the Al_2O_3 coating and the Cu substrate were observed in samples heated to 800 °C, but not in those heated to 700 °C.

The breakdown voltage of the Al_2O_3 coatings does not show significant lowering as the temperature is increased from room temperature to 400–500 °C.

The electrical conductivities of the magnetron-sputtered Al_2O_3 coatings have values that correspond to those of good insulating materials.

The results reveal the potential use of magnetron-sputtered Al_2O_3 coatings on Cu for electrical insulation and oxidation protection of metallic MHD electrode and insulator modules.

Acknowledgements

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