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Author(s)	Ng, HP; Ngan, AHW
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INSULATOR-METAL TRANSITION IN NANOSTRUCTURED Ni-Al THIN FILMS

H.P. NG, A.H.W. NGAN
Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road,
Hong Kong, PR China.

ABSTRACT

The electrical resistance of Ni-Al alloy thin films prepared by dc magnetron sputtering process was found to be abnormally high at room temperature. However, when heated at elevated temperatures, the resistance dropped significantly, exhibiting a remarkable negative temperature coefficient of resistance (TCR). The phenomenon was found to be substrate-independent. Cross-sectional transmission electron microscopy revealed that the films were essentially nanocrystalline and porous in nature. Analysis of the current density-electric field characteristics yielded a satisfactory agreement with either the space charge limited or the Poole-Frenkel models for electrical conduction. The negative TCR effect diminishes and the usual metallic resistance is restored in thicker films, probably due to reduction in particle separation and further coalescence of neighbouring crystallites.

INTRODUCTION

Materials exhibiting insulator-conductor transition have been extensively investigated in the last few decades because of their scientific interest and potential engineering applications. Electrical resistivity of this range of materials will undergo drastic changes under the influence of stress or thermal agitation. It is, for instance, reviewed by Mott that certain metals such as barium undergo band-crossing transition and become insulators under sufficient compression [1]. Some ceramics and transitional metal oxide materials, on the other hand, have conduction mechanisms being sensitive to temperature changes with either positive or negative temperature coefficients of resistance (TCR). Apart from the intrinsic material properties, which give rise to the above striking conductivity transitions, the nano-sized crystalline structure has also been found to have substantial influence on the electrical properties of the materials [2]. Thin films have therefore received much for the effects of their miniaturised crystal size and the correlated short-range ordered (SRO) structure on the behaviour of electrical conduction. In this paper, we report an electrical anomaly observed on our Ni-Al binary alloy thin films. Ni-Al coatings with a 3:1 stoichiometry have been investigated in our previous work with respect to its mechanical strengthening and oxidation protection effects on Ni substrates [3]. Although the Ni-Al alloy films conform to a normal metallic conductivity when the thickness is well above 1 micron, an abnormally high electrical resistance is exhibited at room temperature when the film is thinner than a few hundred nanometers. The electrical resistance ramps down drastically, however, when the film is heated up to a moderate temperature. The aim of the present work is to characterise the negative temperature coefficient of resistance (T.C.R.) observed in the Ni-Al alloy films and to attempt to explain such a behaviour.

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EXPERIMENTAL PROCEDURE

Thin Film Preparation

The Ni-Al thin films were deposited by a water-cooled DC magnetron-sputtering device (Bal-Tec MED020) using a nickel-aluminide alloy target with the 3Ni:1Al stoichiometry. The sputtering vacuum chamber was evacuated to a base pressure of below 1×10^{-5} mbar and a continuous flux of ultra high purity Ar was introduced at a pressure of 2×10^{-2} mbar afterwards. In order to ensure a clean deposit, pre-sputtering of the target was performed for an adequate time period. Pure nickel approximately 15mm×20mm×1mm in size was used as substrates. Prior to depositions, the substrates were mechanically polished and then treated with acetone and methyl alcohol to remove any organic contamination. The Ni-Al films were deposited at a sputtering power of 70W. Although there was no additional thermal source applied to the nickel substrate during the deposition process, the substrates became warmed up to approximately 80°C by the plasma-discharge heating. The thickness of the Ni-Al films was limited to 200nm by means of sputtering time control.

Characterisation of Film Microstructure

Cross-sectional transmission electron microscope (XTEM) specimens were prepared by slicing a cylindrical assembly consisting of two deposited substrates glued together with their films facing against each other. The slices were mechanically polished to a thickness less than 80 microns, followed by twin-jet electropolishing with 90% methanol + 10% perchloric acid at 5V and -50°C. All the XTEM specimens were examined using a JOEL 2000FX TEM operating at 200kV.

Electrical Properties Measurement

The variation of electrical resistance with respect to temperature was measured for the Ni-Al thin films. The deposited specimens were rested, with the films facing downward, on two thin copper electrodes connected to a high accuracy digital ohmmeter (Tektronix DM257). A piece of ceramic block was inserted between the electrodes and the heater surface to facilitate electrical insulation. The temperature of the films was monitored by a surface contact type thermocouple mounted on the top of the specimens. The power of the heater was gradually controlled such that the samples were heated up at a sufficiently low speed to ensure a quasi-steady state.

The J-E characteristics were also measured for the thin films. The deposited specimen was placed in between two copper electrodes, each with an area of 0.78cm^2, under a constant contact pressure of approximately 5×10^3 Pa. The potential difference across the film specimen was monitored by a voltmeter connected in parallel across both the specimen and a high accuracy ammeter.

RESULTS AND DISCUSSIONS

As revealed by the XTEM micrographs shown in Fig.1, the Ni-Al thin film exhibits a pronounced columnar structure, which is a common structure observed in thin films under low

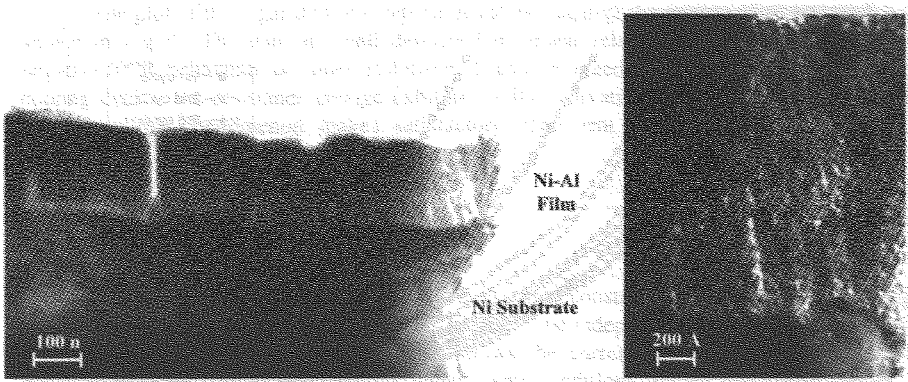

Fig.1 XTEM micrographs showing (a) the columnar structure associated with a Ni-Al thin film sputter-deposited on a Ni substrate at 80°C; (b) the constituent nano-crystals of about 50Å in size.

temperatures. However, the columns are found to consist of aggregation of nano-crystals with size around 50Å. Such a fine crystallite structure is accompanied by an exceptionally high density of inter-granular boundaries, which makes the film porous in nature.

Fig.2a shows the variation of the electrical resistance of the Ni-Al thin film grown on a nickel substrate during a number of sequential heating and cooling processes. It can be seen that the resistance of the film drops from an unmeasurable high level (over 20 MΩ) down to the kilo-ohm range at a decaying speed as the temperature rises to above 200°C. This clearly demonstrates that the conduction in the thin film is associated with a negative temperature coefficient of resistance (TCR), the magnitude of which is describable as an insulator-to-metal transition. Between every heating and cooling curve, a resistance gap is present, and this declines upon cyclic repetitions of heating and cooling until the two curves coincide with one another. This can be interpreted as a consequence of crystallinity enhancement of the amorphous-like structure in the film by thermal agitation, or equally likely, a progressive release of charge carries, which are originally confined to traps, to promote the conductivity. Similar Ni-Al films, which were deposited on silicate glass substrates, have been found to follow a similar electrical behaviour, suggesting that the negative TCR phenomenon of the Ni-Al films is substrate-independent. A supplementary resistance measurement has also been made on a pure nickel thin film prepared under similar experimental conditions. The result shows that the negative TCR effect is, however, negligible in the pure Ni film when compared with the Ni-Al counterpart (Fig.2a).

The extremely low conductivity of the Ni-Al thin film is once anticipated to be due to the formation oxides materials like NiO and Al_2O_3, both of which are essentially insulators at room temperature. Yet it has been well reported that NiO showed hardly any increase in conductivity even well above its Néel temperature (523K) [4]. On the other hand, it would be difficult to imagine that alumina would participate in conduction at elevated temperatures. So it is evident that such an electrical anomaly is largely attributed to the Ni-Al binary system itself. It is also found that the negative TCR effect of the Ni-Al thin films gradually diminishes as the thickness increases. This is anticipated to be a consequence of further crystallite coalescence and the associated reduction in the defect concentration and inter-particulate separations.

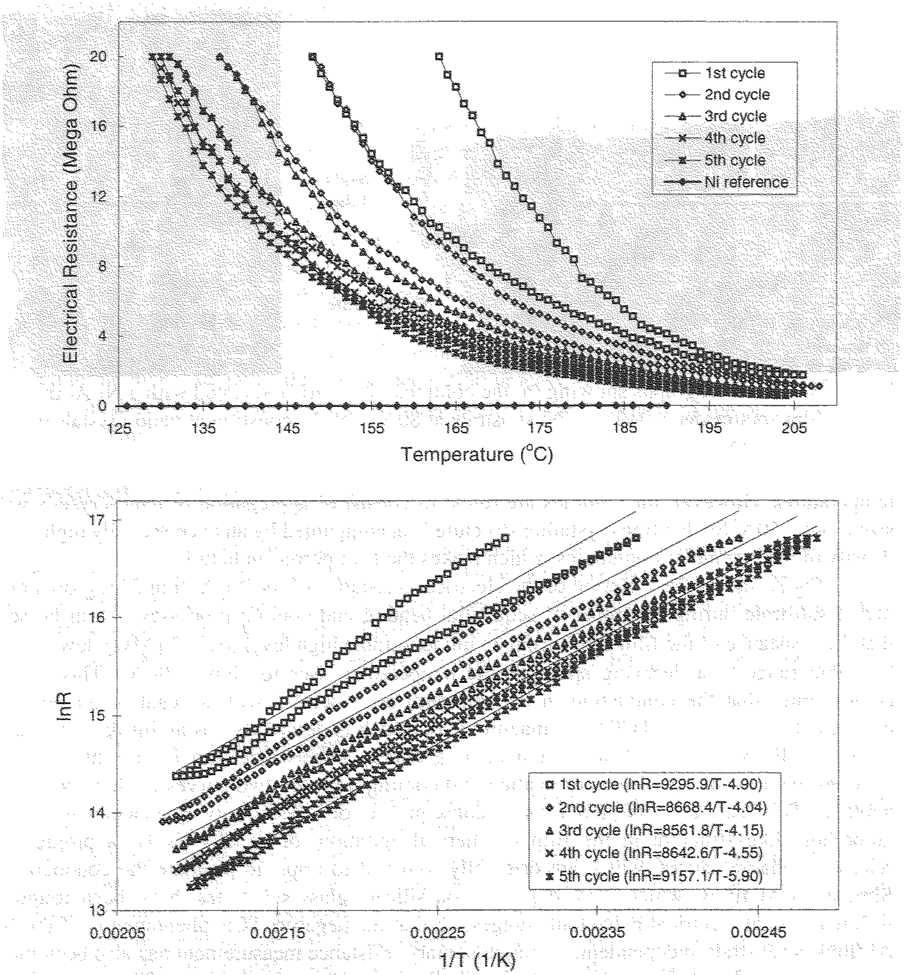

Fig.2 Temperature dependence of electrical resistance of nanostructured Ni-Al thin films: (a) resistance as a function of temperature; (b) lnR-1/T relationship.

The electron transport behaviour has long been investigated by different workers for thin metal films of structures ranged from being discontinuous to continuous [5]. Porous films, being the intermediate type, are believed to possess a complicated conduction mechanism influenced by a number of additional factors, such as intergranular boundary and diffuse scatterings [6]. There has been a tendency to explain the transport in porous film in terms of tunnelling for its lower activation energy involved when compared with thermionic emissions, especially when the porosity is high. It is therefore of interest to know more about the effective conduction mechanisms in our nanostructured Ni-Al films, which show an intrinsic porous nature.

The plot of the logarithm of electrical resistance against the reciprocal of temperature is shown in Fig.2b. The data are well described by linear relationships, especially when the negative TCR behaviour becomes stabilised. It can be noted that, for each of the heating-cooling cycles, the resistance change exhibits similar activation energies of 0.7-0.8eV. This rate-controlling phenomenon makes satisfactory agreement with a simplified thermionic emission model, which is described by:

$$R = C\frac{k}{eT}\exp(\frac{E}{kT}) \qquad (1)$$

where C is a film-dependent constant, k the Boltzmann constant and E the activation energy. Mechanical quantum tunnelling is a process known to be independent of temperature, unless it is otherwise thermally activated [6]. Fig.3 shows the current density (J)-electric field (E) characteristics of the Ni-Al thin films under room conditions, which resembles that of an ordinary semiconductor diode but with a much higher current density level. The J vs E curve can be represented by a polynomial of the forth order, which indicates that a space-charge-limited (SCL) emission mechanism actually takes effect in the electrical conduction. A fairly linear relationship obtained in the log J vs $E^{1/2}$ plot in Fig.4, on the other hand, suggests that the Poole-Frenkel (P-F) themionic emission can also be another effective transport mechanism in the thin films [6]. Summing up the above, it is apparent that the conduction in our Ni-Al thin films is largely facilitated by emission mechanisms, which are successively enhanced at elevated temperatures to facilitate the insulator-conductor transitions. Although adequate evidence to rule out tunnelling conduction is yet to be found, it is believed that, for the Ni-Al films, tunnelling should not be the predominating mechanism as expected in other porous thin film systems.

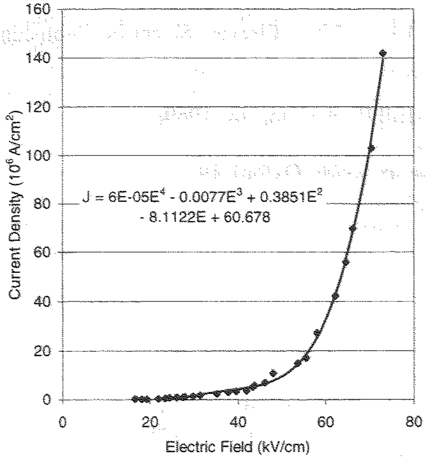

Fig.3. J–E characteristics of a Ni-Al thin film with a negative TCR.

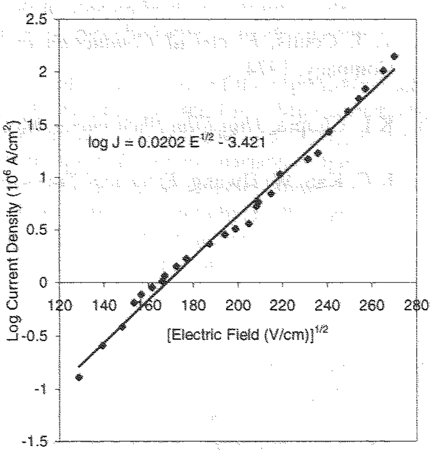

Fig.4. log J vs $E^{1/2}$ plot showing a good agreement with the P-F emission conduction model.

CONCLUSION

In the present study, a striking electrical conduction phenomenon has been detected in sputter-deposited Ni-Al thin films. The alloy Ni-Al films, which are essentially metallic-based, exhibit an inherent insulating property. A large negative TCR was recorded under moderate heating, after which the conductivity approaches metallic behaviour. The insulator-conductor transition is noted to be rate-controlling with an activation energy of 0.7-0.8eV. J-E characteristics of the film shows that conduction models including space–charge-limited (SCL) and Poole-Frenkel (P-F) emissions may be dominating in our thin film systems.

ACKNOWLEDGEMENT

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