Electric Arc Vaporization of Complex Alloys onto Polymeric Films

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ABSTRACT

The works on production of the material for flexible heating elements for temperatures 250-300 °C are reported. The material on the basis of resistive layers of Monel-400 alloy and iron alloy of zero temperature resistivity were produced by the methods of arc vaporization and magnetron sputtering.

Variability of resistive layers adhesion to polyimide films with various adherent underlayers has been investigated at long-term temperature exposure.

In view of obtained results the commercial vacuum deposition equipment have been developed for production of the material for flexible heaters.

INTRODUCTION

Vacuum technology is widely used for the deposition of resistive layers first of all in microelectronics [1]. Recently flexible heating elements are emerging into commercial application. They are produced on the basis of vacuum deposition technologies and other techniques. Advantages of vacuum technologies are accounted for such a tendency. They include capabilities for new materials production, environmental safety, usage of new polymeric materials as substrates, lower costs.

Flexible heating elements, working at the temperature range 200-300 °C, are of a certain interest. However, creation of such elements is connected with many problems: the substrate material, adhesion of the resistive layer to the substrate, heat stability of the element at long-term operation. The present work is dedicated to solution of these problems.

EXPERIMENTAL

The design of a heating element is determined by a set of problems, which should be solved by the created element. For example, for heating of a movable object the heating element of specific power 80 W/dm² is necessary. Current in the heating element will be equal 2 A at maximum supply voltage 40 V, the latter being determined by operation conditions.

Total resistance of the element makes up 20 Ω. At thickness of the resistive layer 3.5 μm and the path width 5 mm current density will make up about 115 A/mm². In this case the heating element temperature makes up 250 °C. The said parameters are determined by the substrate and resistive layer materials.

A polyimide film, as the most heat resistant of known polymeric films, was used as the substrate. The polyimide film behavior at high temperatures determines a ceiling of the heater working temperatures.

It follows from the polyimide chemical structure, that evolution of CO_2 and CO could be a symptom of its destruction. Thus, at temperature 540 °C gaseous products of destruction of film "Kapton-H" make up: CO_2 - 35 %, CO - 58 % [2].

The method of mass spectrometry was used to determine composition of the gases, evolved during the film heating in vacuo.

The film samples were heated in a pyrolytic cell, placed into a vacuum chamber, pumped down to pressure $1 * 10^{-3}$ Pa. The cell was made as a box resistive heater with a chamber 10 * 80 * 100 mm. A film sample 70 * 70 mm was suspended inside the cell chamber. Temperature of the

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heater was controlled by two Chromel-Copel thermocouples. The cell design approximates emissive properties of the heater to those of a “black body”. Thus, stationary temperature of the film sample should approximate to the temperature of the emitter, i.e. the heater.

At the film temperature 70 - 100 °C evolution of adsorbed moisture was observed. The polymer destruction in vacuo begins at temperatures above 370 °C. It was verified by peaks increase from *m/e* = 28 (CO + N_2) and 44 (CO_2). Above 400 °C the destruction process grows very fast.

It is necessary to dry the polyimide preliminary to provide good adhesion. The drying process was carried out in vacuo, winding the film and heating it up to temperature 100 ... 150 °C. As a result of this pre-treatment the contents of adsorbed moisture in the polyimide film was decreased from 3-4 % down to 0 %.

Glow discharge plasma pre-treatment of the film is the second condition for achievement of necessary adhesion. This pre-treatment was carried out in oxygen atmosphere at pressure 7.5 * 10^{-2} mm Hg, discharge voltage 700 V, discharge current 0.2 A. The film was wound at speed 1 m / min.

Monel-400 was used as a material of the resistive layer. A design of the resistive layer was the following: an adherent underlayer and main layer (Figure 1).

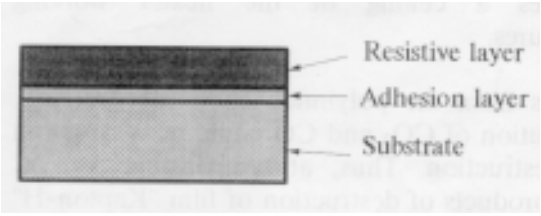


Figure 1. Design of the flexible heater.

The adherent underlayer was deposited by magnetron sputtering of Monel alloy. To adherent layer thickness is 20-25 nm. The main layer was the Monel alloy film, deposited by arc vaporization [3]. Its thickness makes up about 2.7 µm. The electric arc vaporization allows to obtain higher speeds of the film condensation. Above all, this method allowed to avoid high stresses of the coating, which cause curling of produced material. It appeared impossible to avoid such phenomenon during magnetron sputtering [4].

The produced film design had adhesion of metal layers to the polyimide film about 450-550 g/cm. The adhesion was tested by electroplating growth of a copper layer 35 µm thick and subsequent determination of delamination force on a rotatable roller in a tearing machine Instron.

Surface resistance of the obtained film design 2.7µm thick made up 0.3 Ω /□. In case of the main layer thickness 4.0 µm surface resistance was 0.2 Ω /□.

The obtained material has shown high serviceability at temperatures up to 250 °C. When exposing at temperature 300 °C, the adherent underlayer destruction in this material begins after several hundred hours of exposure. The delamination force drops down to zero. We suppose that during long exposure to air at temperature 300 °C the Monel alloy components react with the air components or with the products, evolved from the polyimide. This leads to breakdown of the bonds between the adhesion uderlayer and the polyimide film. This assumption is verified by the spectrometry data, mentioned above.

To increase the temperature limit of the heating element serviceability, the following underlayer materials have been tested:

a) Titanium oxide;
b) Stainless steel;
c) Chromium + Monel;
d) Chromium oxide + chromium + Monel.

The samples with Monel underlayer, deposited by magnetron sputtering, were used as reference samples for comparison with new adherent underlayers.

Main Monel layer 3.5 - 4.0 µm thick was deposited onto mentioned underlayers by electric arc vaporization. Copper electroplating growth was carried out on obtained samples for subsequent adhesion testing. The samples were held in a heating cabinet in the air environment at temperature 300 °C.

Control samples with Monel underlayer showed a sharp decrease of adhesion at exposure temperature 300 °C (Figure 2). The initial adhesion made up 450 - 550 g/cm, it decreased down to 0 after 24 hours. Usage of titanium oxide as the adherent underlayer did not provide necessary initial adhesion (it made up 50 - 100 g/cm). Samples with

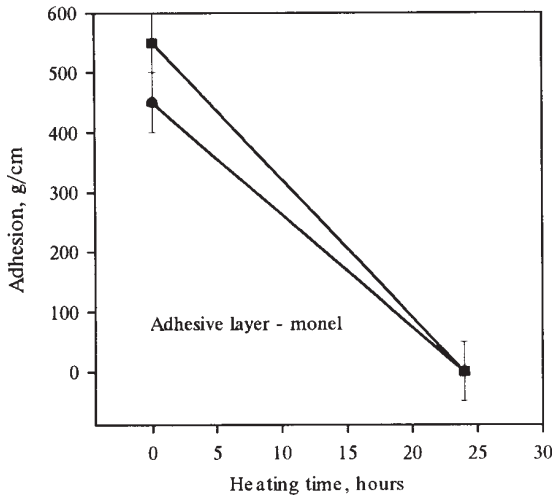


Figure 2. Changes of the resistive layer adhesion at exposure temperature 300 °C (Monel was as the adherent underlayer).

chromium and Monel adherent underlayers had initial adhesion about 850 g/cm, the adhesion decreased down to 200 g/cm after 96 hours of exposure at temperature 300 °C.

Samples with a triple underlayer design (Cr_2O_3 + Cr + Monel alloy) had initial adhesion within 500 ... 900 g/cm, after 750 hours of the temperature exposure the adhesion made up > 300 g/cm.

The best results of temperature stability were obtained with the underlayer of stainless steel 12X18H10T. The initial adhesion of these samples made up from 600 up to 1000 g/cm. After 50 - 350 hours of exposure at temperature 300 °C the adhesion was stabilized at level 500-600 g/cm, after 700 hours of exposure it made up 450 g/cm. It was possible to measure adhesion at level 100 g/cm after 960 hours of exposure (Figure 3).

It is necessary to note that after 400-500 hours of the temperature exposure, it was very difficult to carry out quantitative adhesion measurements. The main reason is that the polyimide film becomes fragile and it is a complicated thing to separate the deposited layer from polyimide. The latter tears and becomes responsible for decreased values of the delamination force.

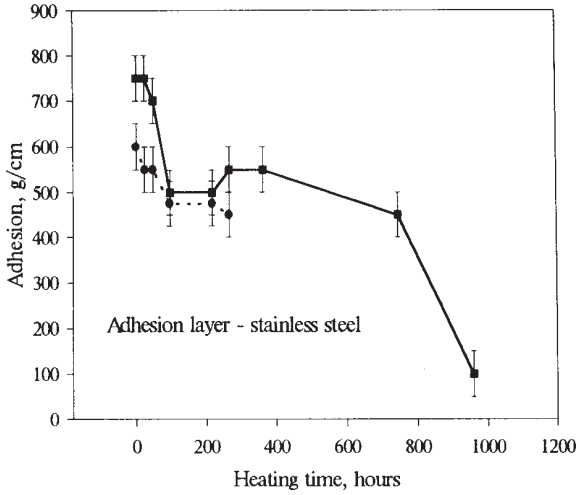


Figure 3. Change of the resistive layer adhesion at exposure temperature 300 °C (stainless steel was as the adherent underlayer).

It is important to emphasize that there are no swelling and peeling of metal layers from the polyimide film during long temperature testing of the samples with the stainless steel adherent underlayer within the whole testing cycle (up to 1000 hours). We have carried out the experiments of using special alloy on the basis of iron with zero temperature resistivity (alloy TCR) as the resistive material.

The coating was deposited on the polyimide film by electric arc vaporization without underlayer deposition. The initial adhesion made up 350-500 g/ cm. After exposure at 300 °C during 750 hours the adhesion was 550 g/cm (Figure 4.).

A pilot vacuum machine has been developed on the basis of the conducted investigations for the manufacturing of the initial material for flexible heating elements. Productivity of the machine is up to 450000 sq. ft/year of the material with surface resistivity 0.3 Ω/□ and 300000 sq. ft/year of the material with surface resistivity 0.2 Ω/□ (Fig. 5). Speed of the material winding is 2... 3 m/min. The vacuum machine is equipped with two radiation heaters: for preliminary heating, drying and outgassing of the film, and subsequent baking of obtained layers after deposition. A glow discharge device is provided for plasma pre-treatment of the film. Magnetron sputtering devices are

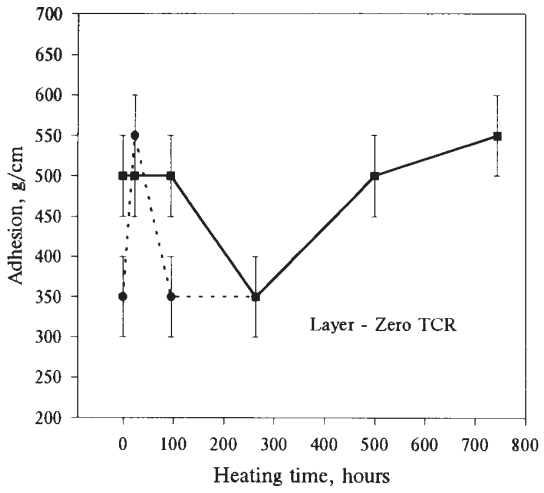
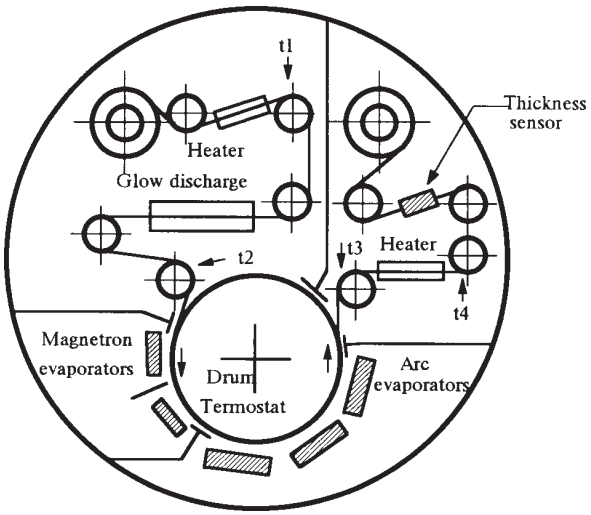


Figure 5. Layout of the vacuum machine for the production of the initial material for flexible heating elements.



provided for the deposition of adherent separating underlayer (stainless steel) and the first layer of resistive alloy.

Planar arc vaporization devices are used for the deposition of the main resistive layer. Special systems of the arc spot control and systems of the spot confinement in case of magnetic materials vaporization provide high uniformity of the coating thickness and target metal yield no less than 80 %.

Investigations of film cooling methods during the deposition of "thick" layers in vacuo have been carried in Sidrabe for more than 20 years [5]. Several methods of film thermostabilization have been developed depending on the density of the heat flow onto the substrate.

Thus, factor of heat transfer between the substrate and the deposition drum was provided at value α = 50 ... 100 W / M² * deg., supplying gas interlayer between them. The value was α = 200 ... 1000 W / M² * deg. and even more, when supplying liquid interlayer. A certain problem remains with the liquid removal from the back side of the film. It could be vaporized during the film baking, removed during polymerization in high-frequency plasma (magnetron) discharge or by other methods of ready-made product protection.

A thermostat of brand new design with cooling gas interlayer is used in the above said vacuum machine. Unhindered deposition of metal layers up to 3 ... 4 μm thick onto polymeric films is provided at a prescribed winding speed.

CONCLUSIONS

Influence of high-temperature exposure on the resistive layers adhesion to the polyimide film have been investigated. The resistive layers were deposited by the methods of arc vaporization and magnetron sputtering.

Technological processes and commercial equipment have been developed to provide manufacture of flexible film heaters for temperatur range up to 300 °C with surface resistivity from 0.2 up to 2 Ω/□.

REFERENCES

1. C.Cabral, Jr., J.M.E.Harper, K.Holloway, D.A.Smith, and R.G.Schad, "Preparation of low resistivity Cu-1 at.% Cr thin films by magnetron sputtering," J Vac Sci Technol A10 (4), 1706 (1992)

2. J.F.Heacock and C.E.Berr, SPE Trans., April, 105 (1965)

3. T. Andronova, A. Vovsi, V. Kozlov, Y. Lipin and O. Rashevic, Deposition of complex composition coatings by the methods of arc vaporization and magnetron sputtering in vacuo, p.39, LATNIINTI, Riga, 1985.

4. T. Andronova, V. Grikite and Y. Lipin, Protective and decorative vacuum coatings, p.61, LATNIINTI, Riga, 1984.

5. A Zeberin. A Kovtun and I. Pipkevich, "On the problem of intensifying heat removal from band substrates in vacuo with the artificial feed of heat exchange gas". In: Physical vapor deposition, p. 91-95, Zinatne, Riga, 1986.