Increasing the adhesion laminated films based on polyimide to the surface

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Abstract. Polyimide film is widely used in various fields of industry, ranging from space technology to microelectronics. The widespread use of the film is due to its high thermal stability, low dielectric constant and good mechanical strength. However, the polyimide film also has a serious disadvantage that prevents its use in a number of applications, namely, a relatively low surface energy, manifested in the low adhesive strength of the film's compounds with other polymers and metals. Currently, a number of surface modification methods of polyimide film are known to improve adhesive properties of the surface without changing the properties of material thickness. The existing methods of polyimide film surface modification can be divided into two large groups: chemical, "wet" methods and "dry" ion-beam and plasma methods. The article presents the results of studies of polyimide adhesion changes depending on the methods of plasma treatment.

1 Introduction

The widespread use of polyimide film is due to its high thermal stability in a wide temperature range (from −270° to +300° C), low dielectric constant and good mechanical strength.

Polyimide film-based laminate is widely used all over the world, which is obtained by applying a layer of copper on one or two sides of a polyimide film. Laminated polyimide film is widely used in the production of flexible printed circuit boards in the aviation, space, military industries, as well as in the production of consumer goods: cell phones, computers, video cameras, etc. In addition, polyimide film is used as cable insulation, in the production of windings of electromagnets, motors, generators. During the production of insulating tape, a layer of varnish is stuck on the polyimide film, then several layers of film are folded and pressed at high temperature. As a result, several layers of polyimide film are glued together.

For the same purposes, it is possible to use a polyimide laminate film and teflon. On the one side, the film is polyimide, on the other, teflon. In the production of insulating tape, the films are folded and pressed at high temperature. The teflon is melted and layers are glued together. However, one of the main problems of this technology is poor adhesion between varnish and polyimide film, teflon and polyimide.

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The modern process of laminated film production includes surface treatment to ensure good adhesion with subsequent coatings, vacuum application of a thin metal layer based on nickel and chromium to ensure good adhesion with a copper coating, vacuum application of a thin copper layer, application of a relatively thick layer of copper by electrolysis. In the most advanced technologies existing in the world, pretreatment of the film allows spraying a thin layer of copper directly onto the polyimide film, bypassing the process of coating the film with an intermediate layer of metal.

2 Materials and methods

The scheme of the ion-beam method of polyimide surface modification is shown in Figure 1. The polyimide film is located in a vacuum chamber pumped to a pressure not worse than $10^{-5}$ Torr. A beam of accelerated ions bombards the surface of polyimide film, provided that a chemically active gas is blown over the surface of the film. Argon ions and oxygen are commonly used as a chemically active gas. The ion energy lies in the range of 0.5-3 keV. In accordance with the existing physicochemical model, it is assumed that as a result of bombardment of the polymer surface with ions, chemical bonds are broken, the interaction of which with molecules of a chemically active gas leads to the appearance of polar groups on the surface, increasing the amount of surface energy.

![Fig. 1. Scheme of the ion-beam method of surface modification in a vacuum chamber.](image)

Figure 2 shows the behavior of surface energy film with an increasing the dose of film irradiation by argon ions in the presence of oxygen [1]. It is shown that as a result of polyimide film processing, its surface energy is increased from 46 to 72 din/cm².
Fig. 2. Dependence of the polyimide film surface energy on the radiation dose.

XPS (X-ray photoemission spectroscopy) analysis of the treated film surface showed that it is formed a new polar groups >C–O–H, –(C=O)–O, –(C=O)–(NH)–. At relatively small doses of radiation, the morphology of the surface is not changed, so the increasing of surface energy is determined by a changing of chemical composition surface. At an irradiation dose of more than 5 × 10¹⁶ ion/cm², the morphology of the surface begins to change towards the surface area development.

A typical scheme of polyimide film plasma treatment at reduced pressure is shown in Figure 3. The film is located inside the vacuum chamber, where a discharge is ignited and plasma is formed. In plasma, the film is exposed to electron and ion fluxes, ultraviolet radiation, as well as radicals of chemically active gases formed during their dissociation. The basic physico-chemical processes occurring during plasma processing are the same as in ion-beam experiments. Thus, in [2] it is reported about the formation of polar groups on the surface of a polyimide film treated with a plasma stream enriched with oxygen atoms. The formation of polar groups is accompanied by a contact angle decreasing and surface energy increasing. It should be noted that the film processing time in plasma is about 1 hour.

Fig. 3. A typical scheme of polyimide film surface modification by low-pressure plasma.

The scheme of polyimide film plasma treatment at atmospheric pressure is shown in Figure 4. The discharge is ignited between the main plasma-forming electrode (metal thread) and a flat grounded metal electrode. The polyimide film can be located directly on a metal grounded electrode or on a dielectric gasket located on a metal electrode. The film is stretched at a constant speed through a discharge in which it is exposed to electrons, ions, ultraviolet
radiation and numerous radicals and molecules formed when an electric current passes through the air.

Fig. 4. The typical scheme of polyimide film surface modification in plasma at atmospheric pressure. 1 – a device for supplying gas to the reaction zone, 2 – a plasma–forming electrode, 3 – a sample, 4 – a metal grounded electrode.

One of the best result in increasing the adhesion of metal layers to a polyimide film treated in a discharge at atmospheric pressure was obtained in [3]. However, in the work [3] performed at atmospheric pressure, the discharge was ignited not in clean air, but when a mixture of argon and oxygen was supplied to the discharge gap, respectively, with a flow rate of 20-30L/min. Each sample was processed for 35 seconds.

The implementation of each of these methods requires equipment of varying degrees of complexity and cost [4-6]. It is obvious that the cheapest and the simplest is the method of polyimide film processing in a discharge at atmospheric pressure, and the most expensive and the most complicated is the ion-beam method [7].

3 Plasma treatment of polyimide-teflon film

The scheme of polyimide film processing in a discharge at atmospheric pressure used in this work is close to that shown in Figure 4. The polyimide film was located above the grounded metal electrode and was moved relatively to the discharge which was supported by the electrode 1. A discharge in the air was used, no additional gases were used. After several scans in the discharge, the film was removed and the contact angle and adhesive force were measured. The contact angle measurement scheme is shown in Figure 5.

Figure 5. Contact angle measurement scheme.

To measure the adhesive force, duct tape was glued to the polyimide film surface, then the force required to tear off the duct tape was measured as shown in Figure 6.
Experiments have shown that there is the dependence of contact angle from polyimide film scans number in an atmospheric discharge. With one-time sample scan by plasma, the contact angle is 70°, but with an increasing of scans number it is decreased rapidly. With an increasing of scans number up to more than 14, the value of contact angle reaches a value of about 20°, and then practically is not decreased. However, the adhesive strength as a result of processing is increased slightly, by not more than 30%.

The review of the literature shows that the best result in increasing the polyimide film adhesion can be obtained in ion-beam experiments using expensive complicated equipment. However, an attempt to do with less expensive methods was made. Therefore, experiments were carried out on polyimide film processing in a discharge at reduced pressure. The task was set to organize the film processing in a discharge at reduced pressure so as to preserve the basic elements of ion-beam processing. For this purpose, the film samples were attached to RF discharge electrodes, next to which there is a quasi-stationary potential jump accelerating the ions towards the electrode.

The discharge was ignited in helium with an admixture of air, ensuring the presence of chemically active radicals in the discharge. The helium consumption was in the range of 10ml/min. The processing time was 1 min. Solid and mesh electrodes were used in the experiments. The obtained results were summarized in Table 1.

<table>
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<th>Sample Number</th>
<th>Processing conditions</th>
<th>Measurements, N/cm</th>
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<tbody>
<tr>
<td>0</td>
<td>Raw polyimide</td>
<td>3.5</td>
</tr>
<tr>
<td>1</td>
<td>Active electrode, solid</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>Passive electrode, solid</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Active electrode, mesh</td>
<td>3.55</td>
</tr>
<tr>
<td>4</td>
<td>Passive electrode, mesh</td>
<td>3.75</td>
</tr>
</tbody>
</table>

4 Conclusion

The experiments have shown that the polyimide film processing in an atmospheric discharge increases adhesion slightly. At the same time, long-term exposure of plasma to the surface is necessary to obtain meaningful results. Ion-beam surface treatment can give the best result. But this method requires quite expensive equipment and means of pumping out the vacuum chamber. The most acceptable result can be obtained in a discharge at reduced pressure. In
this case, the best results were obtained in experiments with polyimide film samples located on solid flat electrodes in a low-pressure RF discharge in helium.

References