

Increase of Gold-Teflon FEP Joint Strength by Electron Bombardment

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Synopsis

The strength of joints between Teflon FEP (Type A) and 500- to 1000-Å gold layers deposited by evaporation can be greatly increased if the Teflon surface is subjected to electron-beam bombardment prior to the evaporation process. Typically, joint strengths of about 60 kg/cm², approaching the bulk strength of Teflon, are obtained for treatments with electron-beam energies in the range of 5 to 20 keV and intercepted charge densities of about 5×10^{-8} C/cm². This compares with gold-Teflon joint strengths of about 10 kg/cm² for untreated material. The increase in joint strength is believed to be primarily due to crosslinking caused by the electron bombardment. Compared to the other known treatments to improve gold-Teflon joints, the present method has the advantage that the charge-storage properties of the Teflon are not irreversibly degraded. It is possible, for example, to store charge densities up to 3×10^{-8} C/cm² on 25-μm films treated with this method, with the same favorable charge-retention properties and thermally stimulated current characteristics as obtained for untreated Teflon.

INTRODUCTION

The strength of gold-Teflon joints obtained by evaporation of gold onto untreated Teflon FEP (Teflon FEP, type A, E. I. du Pont de Nemours & Co., Inc.) surfaces is generally weak. The reason for this is believed to be the presence of surface regions of low mechanical strength on the Teflon. Some surface treatments, such as the CASING process,^{1,2} modify these surface regions and thus strengthen the boundary layers. Adhesive joints formed between Teflon thus treated and gold are, in certain cases, as strong as the bulk strength of the Teflon.

The known treatments to improve adhesive joint strength have, however, a degrading effect on the charge-storage properties of Teflon. Evidence of this is obtained, as shall be demonstrated below, from a comparison of thermally stimulated currents generated by treated and untreated films previously charged. This means that the known treatments for improving joint strength are inadequate for applications where the charge-storage properties of Teflon are important.

In the present paper a new method for treating Teflon to improve adhesion of gold is described. The method consists of the application of electron bombardment of proper beam energy and intercepted charge

density to the Teflon surface. This method has the advantage of causing only limited and, in a certain sense, reversible damage to the charge-storage properties of the polymer.

EFFECT OF ELECTRON BOMBARDMENT ON JOINT STRENGTH

Preparation and Testing of Samples

The sequence of steps necessary to prepare and test the gold-Teflon composites is schematically shown in Figure 1. Nonmetallized 25- μm FEP film (type A) is cut into circular samples 8.6 cm in diameter and framed between two cardboard rings for convenience in handling. These rings leave a circular Teflon area of 7.4 cm in diameter exposed.

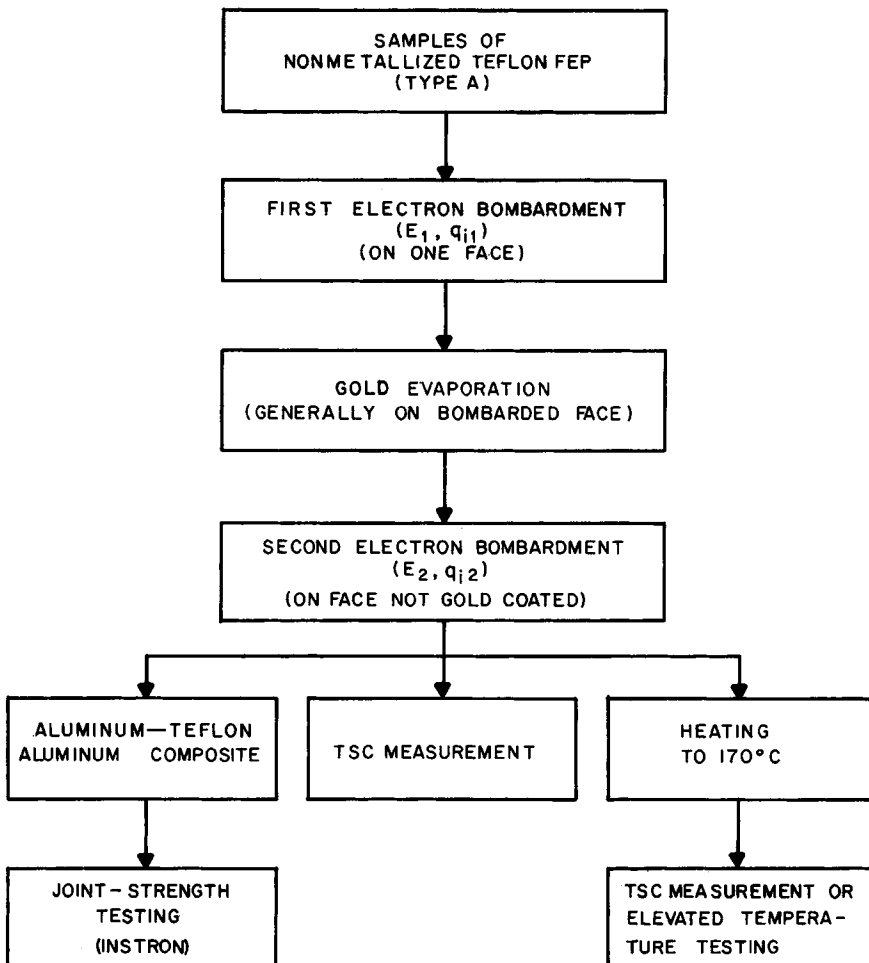


Fig. 1. Flow chart for joint strength testing and thermally stimulated current measurements.

For all but the control experiments, the samples are mounted on metal backplates in the target chamber of an electron-beam accelerator. After evacuation of the chamber, each sample is bombarded with a scanned monoenergetic electron beam³ having an energy E_1 in the range of 2.5 to 40 keV and an intercepted charge density q_{i1} of 10^{-8} to 10^{-5} C/cm². After bombardment, the samples are removed from the target chamber and their stored charge density is measured by noncontacting or contacting methods.⁴ The stored charge density (negative on the irradiated side and positive, but of equal magnitude, on the other face) as a function of the incident charge density is shown in Figure 2. As long as no other experiments are performed with the samples, the stored charge can be considered approximately time invariant.

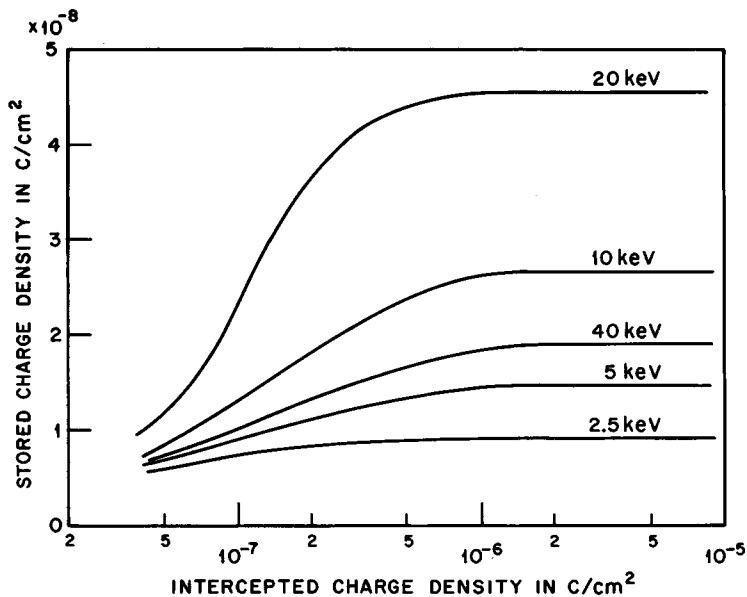


Fig. 2. Stored charge density on nonmetallized 25- μ m Teflon FEP samples as function of intercepted charge density q_{i1} with electron-beam energy E_1 as parameter. The stored charge is negative on the bombarded face of the sample and positive (but of equal magnitude) on the other face.

The samples are then mounted in an evaporation chamber in such a way that only one face of the film (which may be the bombarded or nonbombarded face) is exposed. This face is coated with a gold layer of a thickness of 500 to 1000 Å.

After the evaporation process, the samples are charged on the noncoated face with an electron beam of energy $E_2 = 20$ keV and intercepted charge density $q_{i2} \approx 5 \times 10^{-8}$ C/cm². This second charging (see Fig. 1) is necessary (1) for the successful formation of composites used for joint strength testing and (2) for thermally stimulated current (TSC) measurements.

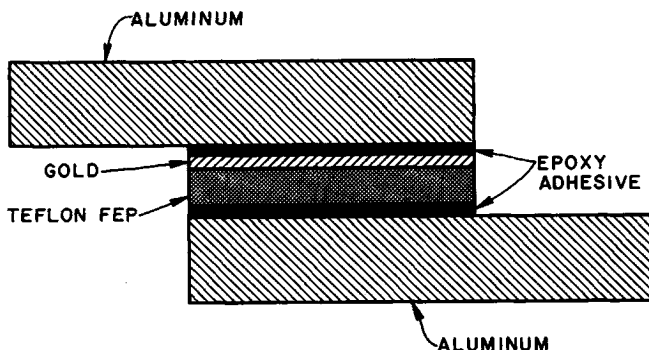


Fig. 3. Schematic cross section of aluminum-Teflon-aluminum composite.

Tensile-shear composites, schematically shown in Figure 3, are formed by cutting strips of $2.5 \times 1.25 \text{ cm}^2$ from the circular Teflon samples and joining both sides of them by means of a conventional epoxy adhesive to $12.5 \times 2.5 \times 0.16 \text{ cm}^3$ aluminum pieces which have been chemically etched. The composites are bonded at 70°C in a special device to maintain a 1.25-cm overlap. After the epoxy adhesive is cured, the composites are tested for joint strength in an Instron (Instron Engineering Corporation, Canton, Mass.; joint strength tested according to ASTM D1002-64).

Results

The adhesive joint strength, measured within a few days after gold evaporation, is shown in Figure 4 as a function of the intercepted charge density with the electron-beam energy as parameter. The results demonstrate that for the samples metallized on the bombarded side ("−" samples, since the negatively charged face is metallized), the adhesive joint strength increases generally with increasing intercepted charge density q_d and also increases with electron-beam energy E_1 up to $E_1 = 10 \text{ keV}$, but drops off for higher energies. Samples metallized on the side facing away from the electron beam during bombardment ("+" samples) show a slight decrease of joint strength with q_d . At q_d values of less than $5 \times 10^{-8} \text{ C/cm}^2$, the joint strength for "−" and "+" samples is approximately the same as for nonbombarded samples (about 10 kg/cm^2). All these results will be discussed below.

Also shown in the figure are results of joint strength measurements on samples metallized on the bombarded side but submerged in ethyl alcohol or water for about 10 min before the metallization was performed. This treatment discharges foils with original charge densities of $2 \times 10^{-8} \text{ C/cm}^2$ to about $4 \times 10^{-10} \text{ C/cm}^2$. As seen in Figure 4 (point A), the joint strength on such samples is the same as on samples not discharged. However, control samples only submerged in alcohol or water and not previously bombarded show poor joint strength (point B in the figure).

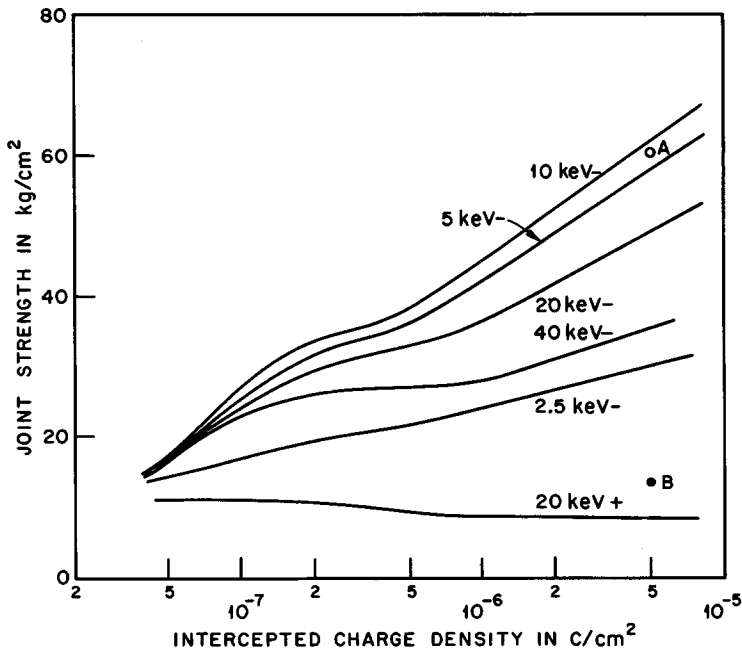


Fig. 4. Tensile-shear joint strength of gold-Teflon FEP interface of composites shown in Fig. 3 as function of intercepted charge density q_{it} with electron-beam energy E_1 as parameter. Thickness of Teflon FEP films is $25 \mu\text{m}$. Point A: Joint strength for sample bombarded with $E_1 = 10 \text{ keV}$ and submerged in ethyl alcohol to remove stored charge before gold evaporation. Point B: Joint strength for sample not bombarded but submerged in ethyl alcohol before gold evaporation.

Joint strength measurements were also performed after the metallized samples had been stored in a laboratory atmosphere for about 8 months. It was found that, contrary to gold-semiconductor systems,⁵ the joint strength does not depend on the duration of storage.

Discussion

A comparison of Figures 2 and 4 indicates that the joint strength on “—” samples increases with intercepted charge density q_{it} even beyond the point where the stored charge density saturates. This suggests that the joint strength is primarily controlled by surface modifications (as discussed below) caused by the electron beam and only to a lesser degree by stored charge. Support for this is found in the above-described submersion experiments which indicate that for high q_{it} values the bond strength is almost independent of stored charge density.

The increase of joint strength with beam energy E_1 up to 10 keV for large q_{it} is an indication that the total energy of the injected particles determines the extent of surface modifications. The drop of the joint strength observed for energies greater than 10 keV suggests, however, that for good efficiency the beam energy has to be deposited in a region close to the sur-

face. This follows from the fact that the energy deposited in proximity to the surface decreases with increasing electron energy due to the increasing range.⁶ Since the joint strength rises very little for $E_1 > 5$ keV, the surface region important for bonding is probably comparable to the electron range at 5 keV, which equals about $0.3 \mu\text{m}$. The surface modification most likely to cause the improvement in joint strength is crosslinking which is related to the absorbed energy.^{2,7} Crosslinking results in improved cohesion of the material.

The experimental results suggest therefore the following tentative explanation of the dependence of joint strength on q_{11} and E_1 : The enhancement of the joint strength of “-” samples with intercepted charge density is primarily due to increased cohesion of the surface layers of the Teflon. The dependence of joint strength on electron-beam energy implies that the surface-layer thickness is about $0.3 \mu\text{m}$.

The hump of the joint-strength curves (see Fig. 4) occurs at intercepted charge densities ($\approx 2 \times 10^{-7}$ C/cm²) at which the stored charge density in Figure 2 begins to saturate. This suggests an effect of the stored charge on joint strength, possibly caused by improved wetting of the Teflon by the gold. The effect is probably not coulombic since the degree of ionization of the gold molecules during the evaporation process is very low. This dependence of joint strength on stored charge, which appears to be at variance with the submersion experiments performed at greater intercepted charge densities (point A, in Fig. 4), supports a similar finding by Kim and co-workers⁸ on autohesion of polyethylene.

The fact that joint strength for the “+” samples is relatively independent of intercepted charge density is consistent with the above picture. For these samples, the absorbed energy is very small since charge injection is caused by a (comparatively weak) potential gradient across the Teflon-backplate interface during irradiation or at the time of removal of the samples from the back plate. This implies that surface modifications in this case are minor and, in addition, limited to a very shallow surface layer.

EFFECT ON CHARGE-STORAGE PROPERTIES

The effect of electron-beam bombardment, CASING, and other processes on the charge-storage properties of Teflon can best be assessed from a study of the thermally stimulated current (TSC) generated by charged films.⁹ Figure 5 shows TSC curves for two groups of Teflon films: group 1 consists of untreated films which are gold or aluminum coated by an evaporation process, while group 2 consists of films gold coated either by evaporation after CASING treatment or by sputtering. All results are obtained by electron-beam charging ($E_2 = 20$ keV, $q_{12} = 5 \times 10^{-8}$ C/cm²; see Fig. 1) the metallized films and then measuring the displacement current between the metal layer of the film and an electrode mounted on the other side of the film at a distance of 0.5 cm.

The gold- or aluminum-coated films of group 1 exhibit their major TSC peak at about 220°C , in agreement with previous results.⁹ The group 2

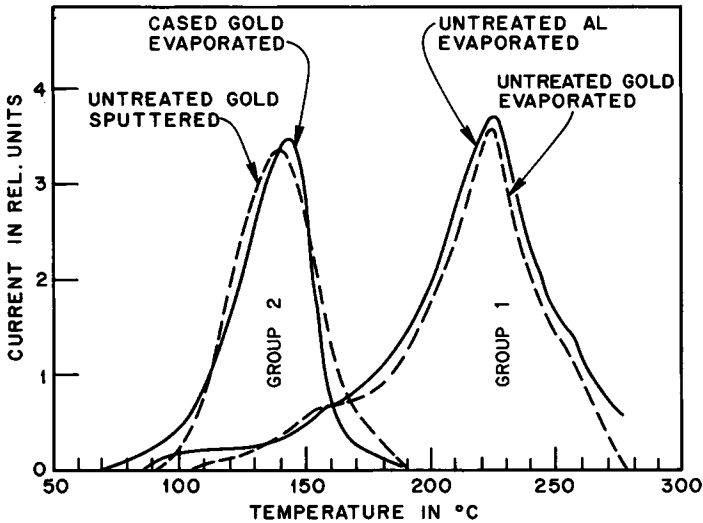


Fig. 5. Typical thermally stimulated current (TSC) characteristics for CASED or untreated 25- μm Teflon FEP samples with gold or aluminum coating. All samples charged with electron beam ($E_2 = 20$ keV, $q_{i2} = 5 \times 10^{-8}$ C/cm 2) before TSC measurements. TSC heating rate: 3.8°C/min.

films, however, show a TSC peak at 140°C, with no higher-temperature peaks present. This indicates that the group 2 films are electrically degraded. It can be shown that this degradation is due to hole conduction caused by the CASING treatment or the sputtering.

A number of TSC curves obtained for films which are electron-beam treated with $E_1 = 20$ keV before gold coating are plotted in Figure 6. As opposed to the TSC curves for CASING-treated films (see Fig. 5), all

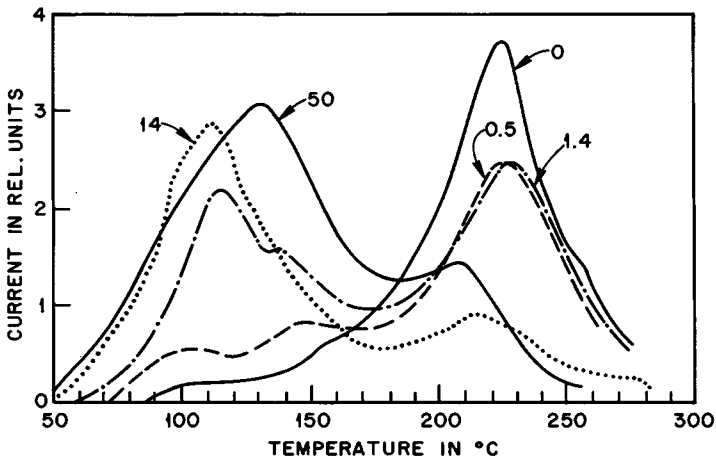


Fig. 6. Typical thermally stimulated current (TSC) characteristics for gold-coated 25- μm Teflon FEP samples. Heating rate: 3.8°C/min. Pretreatment: (1) samples bombarded with $E_1 = 20$ keV and q_{i1} values as shown (in units of 10^{-7} C/cm 2); (2) gold evaporated; (3) charged with $E_2 = 20$ keV and $q_{i2} = 5 \times 10^{-8}$ C/cm 2 .

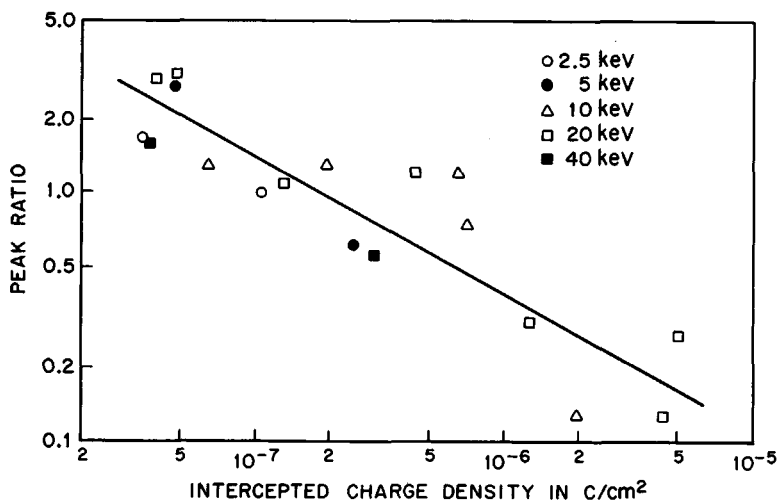


Fig. 7. Ratio of total charge from high-temperature (200°C to 230°C) and low-temperature (110°C to 140°C) peaks of thermally stimulated current characteristic for gold-coated 25- μ m Teflon FEP samples as function of parameters q_{11} and E_1 of electron beam used for treatment prior to gold evaporation. All samples charged with $E_2 = 20$ keV, $q_{12} = 5 \times 10^{-8}$ C/cm² electron beam after gold evaporation.

curves show the presence of a 110° to 140°C peak as well as the 220°C peak. It appears that the population of the low-temperature peak increases with increasing q_{11} at the expense of the population of the high-temperature peak. Similar effects are observed for films treated with other energies E_1 .

This is more clearly shown in Figure 7, where the ratio of populations of high- and low-temperature peaks is plotted as function of q_{11} for a variety of energies E_1 . The populations are simply calculated from the areas under the peaks of the TSC curves. The figure indicates that for values guaranteeing good joint strength, such as $E_1 = 5$ to 20 keV and $q_{11} = 2 \times 10^{-6}$ C/cm², the peak ratio is about 0.3. (This peak ratio can be increased slightly by heating the gold-coated film prior to the second charging to a temperature of 200°C for about 1 hr. Similarly, a slight increase in the peak ratio may be achieved by discharging the film completely and recharging it by a third electron bombardment.)

In order to substantially increase the relative population of the high-temperature peak of such gold-coated films, they are treated as follows: After the second electron bombardment (see Fig. 1) with $E_2 = 20$ keV, $q_{12} = 5 \times 10^{-8}$ C/cm², the charged film is heated in a TSC arrangement (see above) until the dip in current between the two peaks in Figure 6 is reached (about 170°C). Most of the charge carriers in the trap corresponding to the low-temperature peak are then dissipated. Thereafter, the film is removed from the TSC setup.

Further testing proceeds along two avenues. In the first experiment, the films are stored at room temperature for a period of time and then re-

submitted to TSC testing. Results of TSC currents thus obtained are shown in Figure 8. These curves indicate that after ten days no detectable retrapping in the shallow trap that empties at 130°C is observed. The TSC of these films is indistinguishable from that of aluminum-coated films untreated before metallization (see Fig. 5). This indicates that the gold-coated films preheated in the manner described above have the desirable charge-storage properties of aluminum-coated Teflon films.

The second experiment is performed by exposing the gold-coated films, together with some aluminum-coated control samples, to a temperature of 140°C for an extended period of time. The films were shielded from ion sources within the oven.¹⁰ The effect on the measured stored charge density is shown in Figure 9 for two typical films. Both exhibit about the same charge decay. (Similar measurements on other gold-coated Teflon films were taken by A. M. Brzezinski and C. R. Miller, Bell Laboratories; private communication.)

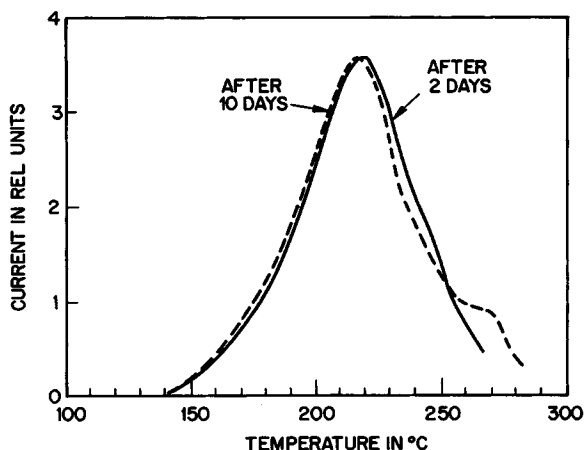


Fig. 8. Typical thermally stimulated current characteristics for gold-coated 25- μm Teflon FEP samples. Heating rate: 3.8°C/min. Pretreatment of samples: (1) bombarded with $E_1 = 10$ keV and $q_{i1} = 2.2 \times 10^{-7}$ C/cm²; (2) gold evaporated; (3) charged with $E_2 = 20$ keV and $q_{i2} = 5 \times 10^{-8}$ C/cm²; (4) heated to dip between the two TSC peaks; (5) stored at room temperature for time indicated.

These experiments indicate that the electrical degradation caused by electron bombardment necessary to ensure a good gold-Teflon joint has no effect on the charge-storage properties of the Teflon film. The only requirement is that the film is first charged to a higher charge density than ultimately needed and then partially discharged until all carriers in the trap corresponding to the low-temperature peak of the TSC curve are dissipated. Films of this kind have, apart from the high gold-Teflon joint strength and the excellent charge-storage properties of untreated Teflon, the environmental advantages resulting from the use of gold as a coating material.

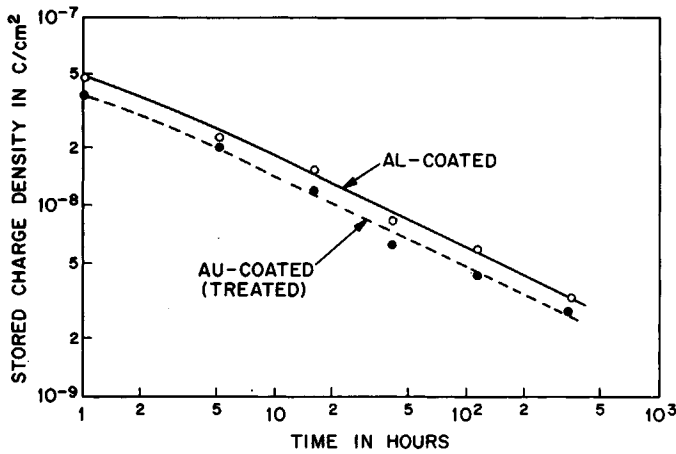


Fig. 9. Decay of stored charge density of gold- and aluminum-coated 25- μm Teflon FEP samples as function of time of storage at 140°C. Pretreatment of gold-coated sample: (1) bombarded with electron beam of $E_1 = 10$ keV and $q_{i1} = 0.75 \times 10^{-6}$ C/cm 2 ; (2) gold evaporated; (3) charged with $E_2 = 20$ keV and $q_{i2} = 5 \times 10^{-8}$ C/cm 2 ; (4) heated to dip between the two TSC peaks.

Teflon films 25 μm thick, for example, can be charged to stored charge densities of up to 10^{-7} C/cm 2 . After removal of the charge carriers residing in the low-temperature trap, the charge density is about 3×10^{-8} C/cm 2 , assuming a peak ratio of 0.3 (see Fig. 7). This charge density is sufficient for most applications of such films. For example, charge densities of only 1 to 2×10^{-8} C/cm 2 are required on Teflon films used in electret microphones.¹¹

CONCLUSIONS

The electron-beam method described in this paper allows one to bond gold and Teflon with a joint strength approaching the bulk strength of the Teflon without degradation of its charge-storage properties. Films of this kind have the advantage that their metal coating is completely inert to environmental conditions. This makes such films useful for application in devices like electret transducers.

The present method promises to be applicable to other coating problems. For example, preliminary tests show that direct evaporation of gold onto alumina substrates results in strong joints if the substrate is bombarded with an electron beam prior to metallization. Such a process may be applicable to the preparation of substrates for integrated circuit applications.

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References

1. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.*, **11**, 1461 (1967).
2. H. Schonhorn, F. W. Ryan, and R. H. Hansen, *J. Adhesion*, **2**, 93 (1970).
3. G. M. Sessler and J. E. West, *Appl. Phys. Lett.*, **17**, 507 (1970).
4. G. M. Sessler and J. E. West, *Rev. Sci. Instr.*, **42**, 15 (1971).
5. K. E. Hag, K. H. Behrndt, and I. Kobin, *J. Vac. Sci. Technol.*, **6**, 148 (1969).
6. M. J. Berger and S. M. Seltzer, *Tables of Energy Losses and Ranges of Electrons and Positrons*, NASA, Washington, D.C., 1964.
7. R. H. Hansen and H. Schonhorn, *Polym. Lett.*, **4**, 203 (1966).
8. C. Y. Kim, J. Evans, and D. A. I. Goring, *J. Appl. Polym. Sci.*, **15**, 1365 (1971).
9. G. M. Sessler and J. E. West, 1970 Annual Report, Conference on Electrical Insulation and Dielectric Phenomena, Washington, D.C., 1971, pp. 8-16.
10. E. W. Anderson, L. L. Blyler, G. E. Johnson, and G. L. Link, *Electrets Charge Storage and Transport in Dielectrics*, The Electrochemical Society, Inc., Princeton, N. J., 1973, pp. 424-435.
11. G. M. Sessler and J. E. West, *J. Acoust. Soc. Amer.*, **53**, 1589 (1973).

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