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FORMATION OF THIN POLYMER DIELECTRIC FILMS
BY ULTRAVIOLET IRRADIATION OF SURFACES IN CONTACT
WITH MONOMER VAPOR

by

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FORMATION OF THIN POLYMER DIELECTRIC FILMS
BY ULTRAVIOLET IRRADIATION OF SURFACES IN CONTACT
WITH MONOMER VAPOR

ABSTRACT: Thin polymer films produced by electron bombardment of adsorbed organic molecules^{1,2} or electrical discharges in organic vapors^{3,4} have recently become useful in fabrication and study of thin-film phenomena and microelectronic circuits.⁵ Ultraviolet irradiation of impactive monomers in the gas phase is known to produce polymeric films on surfaces enclosing the gas.⁶ Recently, it has been shown that direct surface irradiation results in films which have good electrical insulation properties.^{7,8} This report summarizes the results of an investigation of this film process, particularly with respect to films derived from the monomers acrolein ($\text{CH}_2 = \text{CH-CHO}$), methyl methacrylate ($\text{CH}_2 = \text{C}(\text{CH}_3)_2\text{COOCH}_3$), and divinylbenzene ($\text{CH}_2 = \text{CH-C}_6\text{H}_4\text{CH=CH}_2$).

The experimental system consists of a conventional Veeco high-vacuum system and a steel bell jar equipped with sources for thermal evaporation films, a holder for substrates and evaporation masks, and a quartz window for admission of ultraviolet radiation from a mercury arc. The formation of the polymer film is studied by two methods:

1. After evaporation of a metallic film of suitable geometry onto a glass substrate, the surface is exposed to ultraviolet radiation in the presence of a suitable partial pressure of monomer in the bell jar. The illuminated region is defined by a conventional evaporation mask. Evaporation of a second metallic film onto

the polymer produces a set of capacitors. By combining direct physical measurement of polymer film thickness with capacitance measurements, the time average rate of film deposition and electrical properties of the film can be determined.

2. The polymer film is deposited on the illuminated surface of an oscillating quartz crystal, whose change in frequency is related to the mass of material being formed on its surface.⁹ This method enables the instantaneous rate of deposition to be measured, and provides information concerning the mechanism of film formation.

The rate of film deposition is proportional to the partial pressure of monomer up to several mm Hg, and then approaches a constant value.

The growth rate and surface temperature are related by the expression:

$$\text{Rate} = K \exp \left[\frac{\Delta \epsilon}{kT} \right]$$

$\Delta \epsilon$ is positive for all monomers investigated, i.e., the deposition rate increases with decreasing surface temperature. The rate of film growth is proportional to the square root of relative light intensity, and no "dark" growth was detected; the lifetime of "active" sites on the surface was found to be less than 10 milliseconds. By assuming a simple free radical addition polymerization mechanism, a rate law is derived:

$$\frac{dP}{dt} = k_2 \left(\frac{k_1}{k_3} \right)^{1/2} (I_o)^{1/2} [M]$$

which agrees with the data up to relatively high pressures of monomer.

The dielectric constant of the film is approximately that of the bulk polymer, but the dissipation factor is somewhat higher and tends to increase with increasing film thickness. The breakdown voltage is greater than 10^6 volts/cm, as is observed in films whose thickness is less than the average mean free path of an electron in the dielectric. 10^{10} The bulk resistivity is between 10^{10} and 10^{14} ohm cm at low applied fields.

The reliability of the dielectric films, defined as freedom from initial short-circuits due to "pinholes" or voids, is very good above 200 Å and approaches 100% above 500 Å. Thermal cycling between room temperature and 77°K does not appear to affect the capacitors nor does it introduce short-circuits. These qualities, plus long-term stability at room temperature, enable the films to be used as the insulation for complex thin-film circuits, such as thin-film triodes, cryotron loop circuits, and devices for studying tunnel emission, space-charge limited conductivity, and other phenomena in which an extremely thin dielectric barrier is required. The degree of "shadowing" or insulation creep beyond the borders of the illuminated area is less than 0.005" for mask-to-substrate spacing of 0.01" - 0.02", indicating that relatively

high component densities per unit substrate area may be achieved.

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TABLE I
Some Typical Electrical Properties of Polymer Dielectric Films

Monomer	Methyl Methacrylate	Acrolein	Divinyl benzene
Dielectric Constant at 1 kc and 25°C	3.5 ± 0.35	3.5 ± 0.3	3.2 ± 0.2
Dissipation Factor, avg., 500 Å	0.038	0.030	0.005
Dissipation Factor, avg., 4000 Å	0.11	0.09	0.012
Breakdown voltage, v/cm	2×10^6	3×10^6	5×10^6
% samples initially reliable	76% ¹	94%	98%
Stable on thermal cycling, 77° K-298° K	yes	yes	yes
Probable Cross-Linking	uncertain	yes ²	yes

1 Reliable insulation produced only when a photoinitiator was used.

2 Polymer film insoluble in liquid monomer.

FIGURE CAPTIONS

Fig. 1 Logarithm of polymer film growth rate versus reciprocal of absolute temperature of substrate. Monomer: acrolein.

Fig. 2 Polymer film deposition rate versus partial pressure of monomer. Monomer: acrolein.



