SPACE-CHARGE EFFECTS IN VACUUM DEPOSITED POLYIMIDE LAYERS

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Polyimide (PI) thin films were deposited by simultaneous vacuum co-evaporation of pyromellitic dianhydride and oxydianiline monomers, in the ratio 48:52 weight %. The post-deposition thermal treatment made the degree of imidization higher than 40%. Temperature-modulated space-charge-limited current (TM-SCLC) spectroscopy was used to characterize Au|PI|Al sandwich samples. The resulting density-of-states (DOS) function could be described by an exponential energy dependence with a characteristic temperature of 2244 K.

1. Introduction

Polyimides (PI) exhibit an impressive variety of desirable traits: excellent mechanical properties, good adhesion, low thermal expansion, long-term stability, good planarization, low electric permittivity, high breakdown voltage and low dielectric losses over a wide frequency range. PI thin films have proven promising as possible replacements for SiO_2 as an insulator in the future miniaturized multi-level chips for low power consumption and high-speed signal propagation microelectronics.

PI films can be prepared by vacuum co-evaporation of two monomers - pyromellitic dianhydride (PMDA) and oxydianiline (ODA). In this way, the PI deposition can be included in 'all dry' microchip fabrication processes. During the processing, the ratio of the monomers can be changed and films with different morphologies and physical properties can be prepared. Additionally, during the deposition some electronically active material can also be co-evaporated, and a functional composite system can be tailored [1]. The important parameter of materials for electrical applications is the electronic structure of the localised states. This paper aimed to investigate the electronic structure of the localised states in vacuum evaporated PI thin films by temperature-modulated space-charge-limited current (TM-SCLC) spectroscopy.

2. Outline of the theory

When a low voltage (U) is applied to a sandwich sample, an Ohmic current (J stands here for the current density) can be observed:

$$J_{\Omega} = e\mu n_0 \frac{U}{d} ,\qquad(1)$$

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where e is the unit charge, μ the charge carrier mobility, n_0 the free carrier density in thermodynamic equilibrium, and d is the film thickness. At higher voltages, charge carriers can be injected into the sample bulk, and the current can be expressed by the equation [2]:

$$J_{SCL} = \frac{9}{8} \varepsilon \varepsilon_0 \theta \mu \frac{U^2}{d^3},$$ (2)

where $\varepsilon \varepsilon_0$ is the electric permittivity, and $\theta = n_0/(n_t + n_0)$, where n_t is the density of the trapped charge carriers. From Eqs. (1) and (2), one can get the cross-over voltage in the form:

$$U_x = \frac{8}{9} \frac{e n_0}{\varepsilon \varepsilon_0 \theta} d^2.$$ (3)

The dependence of U_x on d^2, called the scaling law [3], is used to check the space-charge-limited current (SCLC) conditions (see Fig. 1).

In the presence of traps distributed in energy, the exponent l of the voltage is higher than two. For example, for traps exponentially distributed in energy, the density-of-states (DOS) function ($h(E)$) can be written in the form:

$$h(E) = \frac{N_t}{kT_c} \exp(-E/kT_c),$$ (4)

where N_t is the total concentration of traps, E is the energy, k is the Boltzmann constant, The exponent l is $(T_c/T)+1$, where T is the temperature and T_c is the characteristic temperature of the distribution. For other types of the distribution (e.g. bell-shaped, Gaussian) l can be voltage dependent [4]. The determination of the DOS function usually consists of a fitting of the measured $J - U$ characteristics on the basis of an *a priori* assumed distribution. This technique is typically an 'integrating' one, and often leads to incorrect results. Therefore, a differential method was introduced. It allows the extraction of an arbitrary DOS distribution directly from the shape of the experimental $J - U$ characteristic [5]. Its temperature-modulated modification (TM-SCLC) allows us to also determine from the experimental data the dominant energy (E_d), i. e. the energy which characterises the occupation of the states. Two equations are used to describe the case [6]:

$$\frac{dn_{sc}}{dE_F} = \int_E h(E) \frac{df(E - E_F)}{d(E - E_F)} = \frac{1}{kT} \frac{\varepsilon \varepsilon_0 U}{ed^2} \frac{2m-1}{m^2} \left[1 + (2 + 3m)B + \frac{dln(1 + B)}{d(lnU)} \right],$$ (5)

where n_{sc} is the density of the space charge, $f(E-E_F)$, is the Fermi-Dirac occupation function, $m = dlnJ/dlnU$ and $B = - [dm/d(lnU)] / [m(2m-1)(m-1)]$. The function $h(E)$ can be determined after deconvolution [7] of the integral in Eq. (5). The E_d can be determined using the equation:

$$E_d = E_b - E_{Fo} = E_a + kT \frac{3 - 4m}{m(2m-1)(m-1)} n + \frac{1}{1+B} \frac{dB}{d(1/kT)},$$ (6)

where E_b is the energy of the mobility edge, E_{F0} is the extrapolated position of the Fermi level at zero temperature, $E_a = d(\ln J_{sc}) / d(1/kT)$ is the experimentally accessible activation energy of the current, and $n = - d(E_a / kT) / d(\ln U)$.

3. Experimental details

PMDA and ODA monomers were simultaneously evaporated in a vacuum of 1×10^{-3} Pa onto planetary rotated (30 r.p.m.) soda-lime glass substrates with previously prepared bottom gold electrodes. In this way, polyamic acid could be prepared. PI films were formed later, by thermal

treatment (500 K for 1 hr). An aluminum top electrode was then vacuum evaporated. The resulting Au|PI|Al sandwich structures, with thicknesses ranging between 100 and 1000 nm, were again thermally treated at 450 K for 4 hrs, to make the metal/polymer contacts more effective. The J - U characteristics were measured at room temperature in a vacuum of 1 Pa, using a computer controlled Keithley 617 electrometer. The DOS function was reconstructed from the experimental TM-SCLC characteristics by the procedure described in detail elsewhere [8].

PI films for SEM and FTIR characterization were prepared in a similar way. SEM imaging of the film surface was carried out with a Philips 515 scanning electron microscope. The PI films for FTIR measurements were deposited on KBr substrates and measured using a Perkin-Elmer 2000 spectrometer. The degree of imidization (conversion from polyamic acid to polyimide) after thermal treatment was determined by comparing the 1380 cm^{-1} peak intensity normalized to the 1500 cm^{-1} peak intensity. This procedure is explained in detail elsewhere [9].

4. Results and discussion

4.1. Characterization of film and electrode quality

The surface morphology of a representative sample, 500 nm, thick is shown in Fig. 1, left. The film has a smooth and defect-free surface. The degree of imidization determined by FTIR spectroscopy was found to be higher than 40%. This value is in agreement with our previous investigations [9].

The verification of the SCLC conditions was performed by checking the scaling law. According to Eq. (3), the U_x vs. d^2 (shown in Fig. 1, right) must be linear, as was observed.
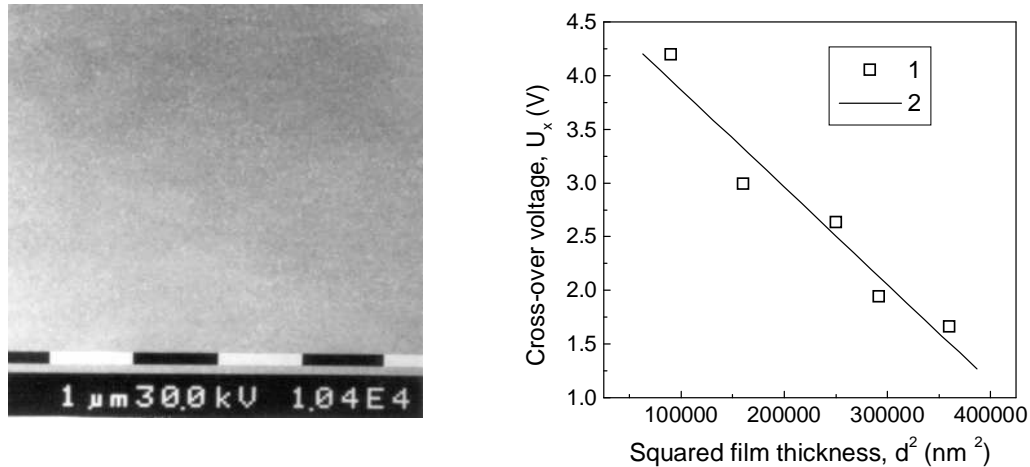

Fig. 1. Left - SEM micrograph of 500 nm thick PI layers, deposited on planetary rotated substrates, thermally treated for 60 min at 500 K. Right - SCLC scaling law: 1- measured points, 2- linear fit.

4.2. Temperature modulated space-charge-limited current spectroscopy

The TM-SCLC characteristics are presented in Fig. 2a. Curve 1 represents the J - U characteristic for a 500 nm thick sample (J was recalculated for the electrode area of 1.3 mm^2). At low voltages, Ohmic current was observed. The short part of the characteristic between 2.5 and 9 V with a slope of 2 indicates a SCL current. Beyond 9 V, the characteristic is obviously superlinear. As the Ohmic current does not carry information about the DOS, it must be subtracted from the overall current before the DOS calculation. The E_a - U dependence (Curve 2) decreases regularly with increasing voltage. This demonstrates a shift of the Fermi level towards the corresponding transport band, as the result of the increased concentration of injected charge carriers. The calculated DOS

(Eq. (5)), plotted as the function of E_d (Eq. (6)), is given as Curve 1 of Fig. 2b. The distribution is close to an exponential one. From the linear approximation (Line 2) on the semilogarithmic scale, the characteristic temperature was determined as $T_c = 2244$ K.
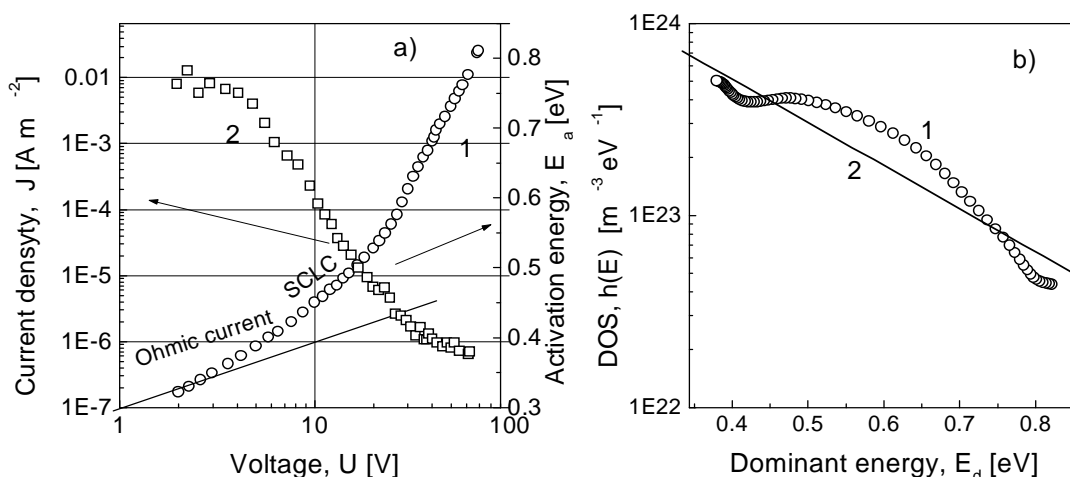

Fig. 2. a) Typical TM-SCLC characteristics for a Au|PI|Al structure. Curve 1 – J vs. U, Curve 2 E_a vs. U ; b) DOS function 1 – calculated from the characteristics in Fig. 2a using Eqs. (5) and (6), 2 – linear fit.

5. Conclusions

The deposited PI films exhibit smooth and defect-free surfaces. Post-deposition thermal treatment of the films yields a degree of imidization higher than 40%. The electrodes of Au|PI|Al sandwich structures show good injecting properties; so that the condition for SCLC is fulfilled. The TM-SCLC characteristics show that the charge transport properties of polyimide films are influenced by traps, exponentially distributed in energy. The analysis gives the characteristic temperature of the distribution as $T_c = 2244$ K.

Acknowledgments

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