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Bioelectrochemistry 66 (2005) 49–53

Bioelectrochemistry

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Integrated circuits protection with the Langmuir–Blodgett Films

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Received 15 January 2004; received in revised form 7 April 2004; accepted 27 April 2004
Available online 26 October 2004

Abstract

Integrated circuits (ICs) can be protected from the environment with the encapsulating polymer layer. Protection properties of such a polymer barrier-layer depend strongly from the structure of thin region where polymer stays in direct contact with the IC surface. One of the interesting questions is how thick should this interphase film be to assure good environmental protection to the IC conductor lines, preventing from their corrosion and failure. In order to answer this question a set of electronic testers with Al conductor lines were modified with 1, 20, 50 multilayers of stearic acid molecules deposited in the Langmuir–Blodgett (LB) transfer method. Next, the electronic testers were subjected to the highly accelerated aging conditions (100% relative humidity (RH), 100 °C) for a period of up to 800 h and conductor lines resistivity changes were monitored. Electronic testers modified with 20 multilayers of stearic acid were better protected from the accelerated aging conditions than the testers modified with 1 monolayer or 50 multilayers. Obtained results suggest that the thickness of the interphase region separating IC surface and polymeric film should be in the range of 10 nm.

Keywords: Encapsulation; IC protection; Interphase region; LB film; Passivation layer

1. Introduction

Electronic integrated circuits (ICs) can be protected from the environment with encapsulating polymeric layer. Encapsulating polymer had to fulfill several conditions—electrical and mechanical. Electrical properties like high resistivity, low content of ionic impurities and low dielectric constant value will be not discussed here. However, the mechanical properties, closely related with the polymer barrier protection like good adhesion to the substrate, low water uptake value, low permeability of water vapors and rheological properties, are closely related with the thickness of encapsulating polymer film. Thicker film does not always mean better environmental protection, its easier delamination, separation and loss of protection barrier properties can rather be expected. Similarly to the phenomena observed in the paint industry, coating applications, sensor film layer, composite materials, protection properties and good adhesion are closely related with the thin interphase layer separating two adhering materials (IC and encapsulating polymer). How thick should this layer be? Sometimes it is claimed that for good environmental protection, several monolayers or even one coupling monolayer thick film are enough to assure good adhesion and proper barrier properties [1–5]. Construction of thin film on the electrode surface, which can assure both environmental protection and proper electrical properties is an important question not only for the IC encapsulation but also for the sensors construction. How thick should the sensor active layer be? A too-thin layer can be easily delaminated or mechanically removed form the sensor's surface. A too-thick active layer can show unacceptable long delay in the electrochemical response or can be too insensitive to the variations of studied species concentration. One can

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doi:10.1016/j.bioelechem.2004.04.010

Table 1
The electrochemical parameters of cyclic voltammogram of free and modified MB in 0.1 M phosphate buffer solution (pH 7.0) at scan rate of 35 mV/s

	E_{pc} (V)	E_{pa} (V)	$E^{\circ\prime}$(V) (vs. Ag/AgCl)	ΔE (V)	Γ (mol cm^{-2})
In solution[a]					
MB	−0.219	−0.191	−0.205	0.028	–
MB+DNA	−0.226	−0.191	−0.209	0.035	–
In membrane[b]					
DNA–MB/PAA/AuE	−0.248	−0.212	−0.230	0.036	2.78×10^{-10}
HRP/DNA–MB/PAA/AuE	−0.247	−0.204	−0.226	0.043	2.10×10^{-10}

[a] In this case, 0.1 mM methylene blue, 0.2 mg/ml DNA and 0.2 mg/ml HRP were used.

[b] The membrane prepared by using 2 mg/ml DNA, 0.2 mM methylene blue, 1 mg/ml HRP and 1 mg/ml PAA.

also expect that better environment protection means also better chemical (or electrochemical) stability. In this paper, we have decided to test how thick should be the thin film deposited in the Langmuir–Blodgett (LB) transfer method to protect Al conductor lines from the corrosion developed during the accelerated aging conditions (Table 1).

2. Experimental

Electronic testers “Tester 5 PW ITE” mimicking real Integrated Circuits (Fig. 1) were mounted in standard DIP-40 package.

Each tester had several triple-track testers, each one with three meandering Al conductor lines (structures: TT3, TT7,

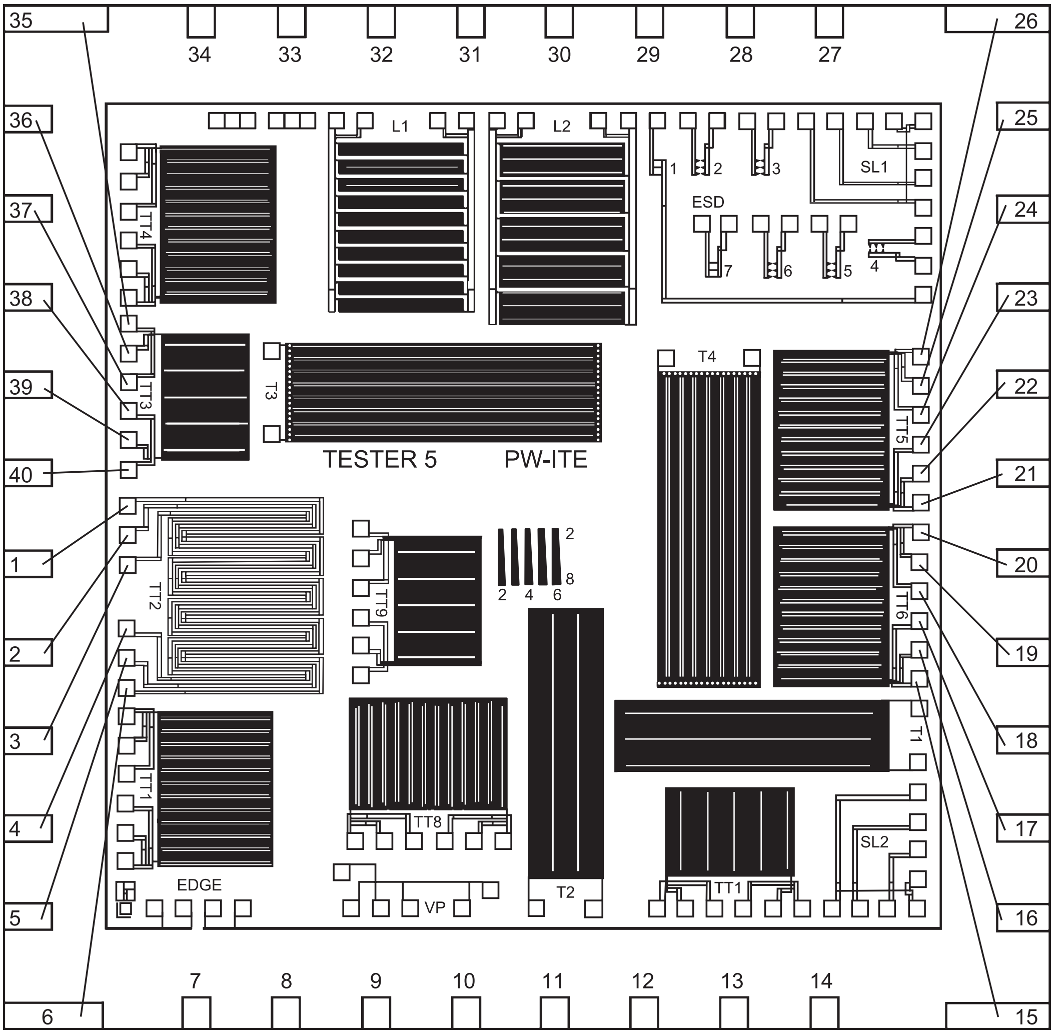

Fig. 1. Electronic tester “Tester 5 PW ITE” made on 6260×6260 μm Si chip with Al metallization.

TT9; line width, 4 μm; spacing between lines, 4 μm; conductor line resistivity about 5700 Ω; structures: TT1, TT4, TT5, TT6, TT8; line width, 10 μm; spacing between lines, 10 μm; conductor line resistivity about 1750 Ω; structure: TT2, line width, 25 μm; spacing between lines, 25 μm; conductor line resistivity about 470 Ω). Testers were UV/ozone-cleaned and next, LBT-coated, respectively with 1, 10, 20 and 50 monolayers of stearic acid (Lauda Film Balance, model FW 2, Z transfer mode) [6]. In the same LB conditions, Si wafers were also coated respectively with 1, 5, 10, 20, 30 and 50 stearic acid monolayers. These wafers were used for characterization of LB-deposited multilayers—water contact angle measurements (sessile drop) and thickness measurements (ellipsometry method).

Electronic testers with deposited 1, 10, 20 and 50 stearic acid monolayers were subjected to the electrical measurements. We have measured resistivity of triple-track testers, impedance and number of “live” structures before modification, after modification and after around 50, 150, 350, 450, 650 and 850 h of accelerated aging conditions (Pressure Cooker Test, 100% relative humidity (RH); 85 or 100 °C). Special lab stand and software procedure was developed for these data collection [7].

3. Results and discussion

Fig. 2 presents contact angle values measured for LB-deposited stearic acid monolayers onto Si wafers. Fig. 3 presents results of thickness measurements of the same LB modified Si wafers.

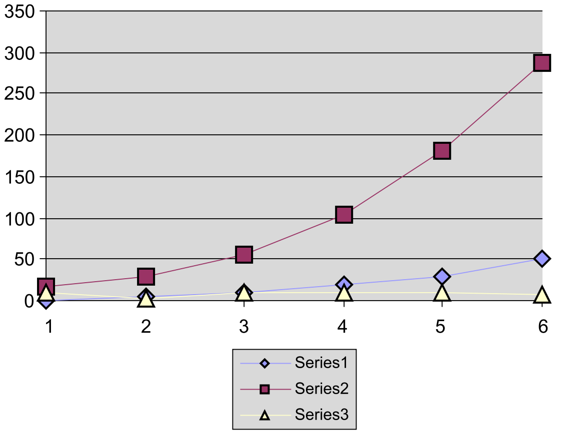

Fig. 2. Water contact angle values for LBT-modified Si wafers.

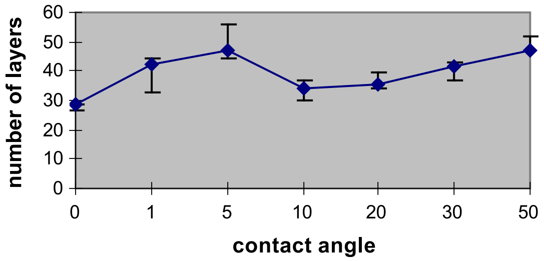

Fig. 3. Thickness of LBT-deposited stearic acid monolayers onto Si wafer.

These results show much lower values both for the water wettability and monolayer thickness than the literature data [6,8] and suggest poor transfer ratio or poor quality of deposited multilayers. Nevertheless, they indicate that some thin films are formed on the Si wafers and we have assumed that roughly the same films were deposited onto Al triple-track testers. In this part of our research, we were more interested whether any changes can be observed in the protection properties of thin films than in the real values of these films. The numerical values of obtained especially thickness measurements are treated only as a rough estimation of thin film modifying Al triple-track testers. It is well known that electronic structures can be modified by deposition of monolayer film by chemisorption (self-assembly method). However, we can obtain in this manner only a single-molecule thick film. To obtain multilayer films by self-assembly requires chemical modification of terminal group in the already chemisorbed monolayer, so self-assembly process can be repeated. There are several methods to obtain multilayer films by repeated chemisorption steps (oxidation of terminal vinyl group, hydrolysis of terminal ester group, sorption of polyelectrolytes) [9]. However, we have decided not to use these methods because preparation method could be harmful to the testers' Al bonds and wirings or obtained films (polyelectrolytes) would not be insulators. This is why we have decided to use LB-deposited films although we were aware of the poor quality of obtained films. Next, the LB-modified testers were subjected to the accelerated aging conditions. There were six testers “Tester 5 PW ITE” with each modification—it means there were six testers without modification (blank ones): six testers with 1 monolayer, six testers with 10 monolayers, six testers with 20 monolayers and six testers with 50 monolayers. Unfortunately, the first set of six testers (with 10 monolayers) had poor quality DIP-40 holders for keeping them in the PCT conditions and this set of testers was destroyed during the first 24 h of aging. After replacement of DIP-40 holders, the aging procedure was completed with unmodified testers (blank) and for testers modified with respectively 1, 20 and 50 monolayers. Up to the first 348 h of aging testers were kept in the PCT conditions with lower temperature (100% RH, 85 °C). In order to accelerate corrosion changes for the next hours up to 850 h, testers were kept in the harsher conditions (100% RH, 100 °C). Resistivity values of unmodified testers were assumed as reference values. The following figures present resistivity changes (in percentage (%)) of LB-modified testers in reference to the unmodified testers before PCT treatment. We were comparing data collected for triple-track testers TT2 (conductor line width of 25 μm and 25 μm spacing between lines); TT5 and TT6 (respectively, 10 and 10 μm) and in two cases, TT3 (respectively, 4 and 4 μm). Data collected for TT3 tester modified with LB-deposited 1 monolayer were too much scattered. Figs. 4–6 present

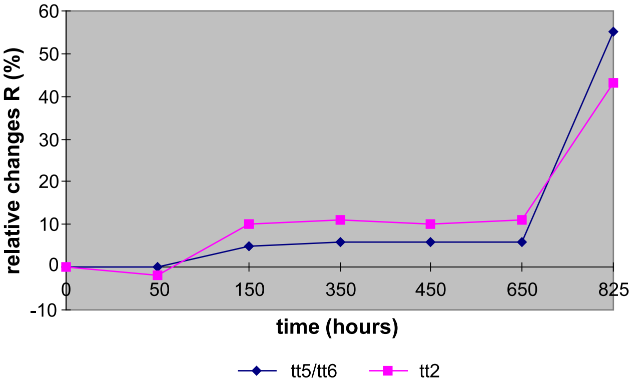

Fig. 4. Relative changes of resistivity for different PW ITE 5 tester structures covered with 1 monolayer of stearic acid in LBT process, during the Pressure Cooker Test (85°C/100% RH/348 h, next 100°C/100% RH).

results of the average resistivity changes observed for the testers listed above modified with 1, 20 and 50 monolayers during accelerated aging.

In Figs. 4–6, the resistivity changes of Al conductor lines during accelerated aging show the same "bath curve" pattern. Relatively small resistivity changes up to the 650 h of aging are followed by the rapid increase in conductor lines resistivity. It is well known that the Al surface during oxidation is passivated with well-adhering layer of alumina oxide. This passivation layer is very effective in delaying the oxidation process and even unmodified testers show stable (plateau region) resistivity increase up to over 500 h of aging (unpresented data). However, for the unmodified testers, this plateau region reaches around 60% of the resistivity increase. It means that unmodified Al testers subjected to the accelerated aging conditions are very stable and "alive" but at the expense of high-resistivity increase of conductor lines. Al conductor lines in unmodified testers are quickly surrounded with dense, stable passivating layer, which "consumes" (oxidizes) huge part of conducting wires, and therefore, strong increase in their resistivity is observed. For testers modified with 1 monolayer (Fig. 4), this plateau region reaches only around 10% of the resistivity increase. For testers modified with 20 monolayers (Fig. 5), this plateau region is around 0% of the resistivity increase, and for testers modified with 50 monolayers (Fig. 6), this plateau region is around 2–10% of the resistivity increase. These results indicate that LB-deposited stearic acid monolayers have influence on the properties of Al oxidation process. Probably this influence of LB-deposited monolayers can be attributed to the "sealing" of the porous alumina oxide-passivating layer, making it less permeable to corroding water and oxygen molecules. Moreover, thinner, "sealed" oxide layer is required to form satisfactory passivating film well-protecting Al wires from their further oxidation. Thin film composed of 20 stearic acid monolayers is more effective in the corrosion protection of Al conductor lines than 1- or 50-monolayer-thick film. Similar conclusions can be drawn from the impedance measurements [7]. From Fig. 3, it can be concluded that 20-monolayer LB film is about 10-nm thick. Thin film of that thickness seems to be the most efficient passivating film for the corrosion protection of Al conductor lines. We have to keep in mind that in these experiments, we had used for metal passivation thin stearic acid film with two features. First one, we had only LB-deposited film, without chemical bonds between Al and deposited film. Secondly, quality of this film was poor. These two facts may suggest that for better organized monolayer films with stronger interaction with conductor surface (for example a self-assembly deposited monolayers), one may expect that even thinner films may yield good corrosion protection for the IC surfaces.

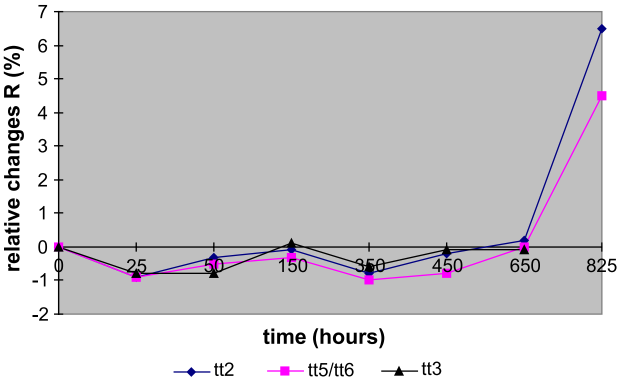

Fig. 5. Relative changes of resistivity for different PW ITE 5 tester structures covered with 20 monolayers of stearic acid in LBT process, during the Pressure Cooker Test (85°C/100% RH/348 h, next 100°C/100% RH).

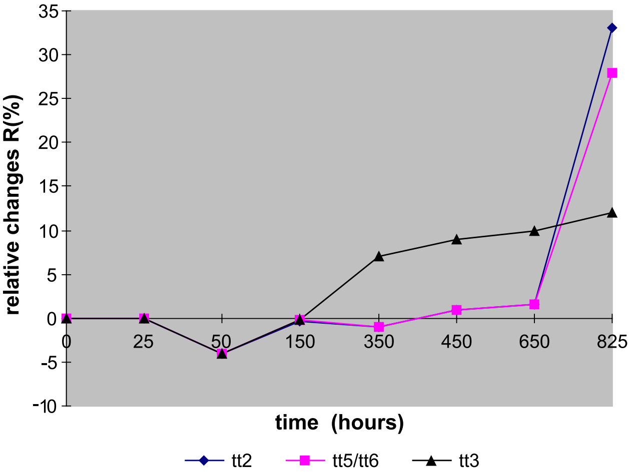

Fig. 6. Relative changes of resistivity for different PW ITE 5 tester structures covered with 50 monolayers of stearic acid in LBT process, during the Pressure Cooker Test (85°C/100% RH/348 h, next 100°C/100% RH).

4. Conclusions

LB-deposited thin films composed of 1–50 stearic acid monolayers have impact on the corrosion protection of Al conductor lines in the IC testers. The strongest effect was presented by the thin film with the thickness of about 10 nm, which corresponds to the 20-monolayer-thick film. This results indicate that organized thin films with the thickness between 1.5 and 23 nm show proper balance between adhesion to the substrate and cohesion within the film, yielding good corrosion protection for metal conductor lines.

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