

CORROSION-PROTECTIVE COATINGS DEPOSITED BY THE PE-CVD METHOD UNDER ATMOSPHERIC PRESSURE

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A b s t r a c t. Protection against the aggressive action of environment is an important problem in the manufacture of integrated circuits. For this reason an extensive search has been carried on to develop thin, well adhesive corrosion-protective coatings, capable of competing with generally used epoxy resins. This study has been devoted to SiO₂ coatings deposited under atmospheric pressure by the PE-CVD method from tetramethoxysilane (TMOS) used in the mixtures of TMOS + Ar or TMOS + Ar + O₂. The coatings were deposited on aluminium printed circuits (testers) and aged at 121°C and 100% relative humidity. The process enables to observe the stability of the coatings, and the changes in electric resistance of the circuits reflect the development of corrosion.

K e y w o r d s: thin film, corrosion-protective film.

INTRODUCTION

The studies on obtaining corrosion-protective coatings, deposited by the PE-CVD method, were the preliminary step of investigation on application of thin films obtained from silicoorganic compounds. The aim of these studies was to determine the possibility of using such films as protective coatings for integrated circuits. Tetramethoxysilane (TMOS) has been chosen as the starting material, owing to its ease of yielding thin films of composition close to SiO₂ at ambient temperatures under atmospheric pressure. The coatings were deposited from the mixtures TMOS +Ar or TMOS+Ar+O₂ containing 0,0056%, 0,4% or 3,2% of oxygen.

EXPERIMENTAL

The studies were performed with the use of experimental circuits (testers) developed in co-operation between Warsaw University of Technology (R. Jachowicz and W. Fabianowski) and Institute of Electronic Technology in

Warsaw (J. Łysko). A silicon integrated circuit with aluminium conducting paths (denoted by the symbols TT2, TT3 and TT//TT6, Fig.1) has been fixed, by means of an epoxy resin, on a ceramic plate [1].

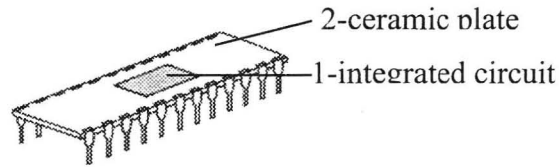


Fig. 1. Tester, 1-integrated circuit, 2-ceramic plate.

The aluminium circuits have different path widths, different separation between the paths, and different electric resistance (Figs. 2 and 3). The testers used in our studies are analogous ATC 01-f 04 testers developed and used in Sandia National Lab USA. The Al path thickness was identical in all the structures used ($0.2\mu\text{m}$).

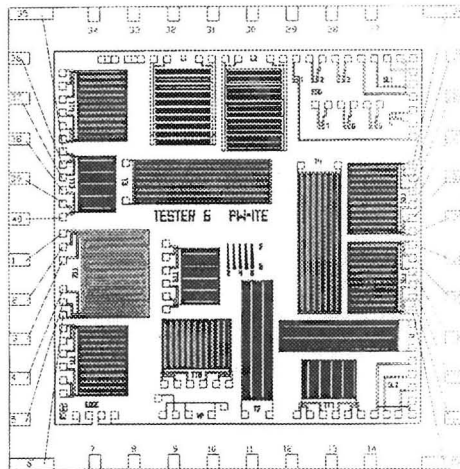


Fig. 2. PW and ITE tester with test circuits (top view) [1]

TT2 structure – path width $25\mu\text{m}$, path separation $25\mu\text{m}$ (3 circuits), elec. resistance about 470Ω ;

TT3 structure – path width $4\mu\text{m}$, path separation $4\mu\text{m}$ (3 circuits), elec. resistance about 5700Ω ;

TT5/TT6 structure – path width $10\mu\text{m}$, path separation $10\mu\text{m}$ (3 circuits), elec. resistance about 1750Ω .

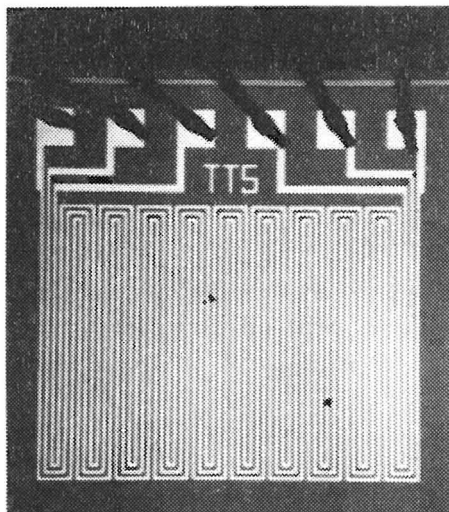


Fig. 3. Test circuit TT5.

The protective film was deposited on the tester surface from TMOS mixtures with argon and oxygen, with variable time of deposition. The constant parameters of the process were: frequency 5 kHz and substrate temperature 25 °C. The process was carried out in a reactor shown in Fig. 4 [2].

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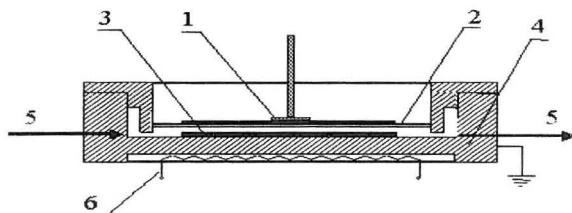


Fig. 4. Reactor for thin film deposition: 1 - High voltage electrode, 2 - Dielectric barrier, 3 - Substrate, 4 - Grounded electrode, 5 - Gas flow direction, 6 - Electric heater.

Thin films deposited from mixtures of TMOS + Ar, TMOS + Ar + 0,056% O₂, TMOS + Ar + 0,4% O₂ and TMOS + Ar + 3,2% O₂ were obtained at room temperature at atmospheric pressure, with TMOS content in argon = 0.33 %. The deposition time was 3, 5, or 10 min.

The passivating properties of the films were evaluated in a series of measurements, in which they were exposed to the action of temperature 121 °C in air of relative humidity 100 %. At specified intervals the testers were cooled, the number of samples not destroyed was determined, and the changes in resistance of

the circuits were measured with a precision of 0.05%. For comparison an identical ageing test was performed with identical testers having no protective coating and with testers protected with the epoxy resin HYSOL FP 4511 produced by Dexter, which is generally considered as the most effective protective agent for such type of circuits. In order to determine, how the process of ageing affects the stability of the circuits tested, the resistance of the testers was measured at definite time intervals. The measurements enabled to determine the fraction of paths that survived the process of ageing. The protective ability of the coatings were determined by the percentage of unaffected aluminium paths and by the change in electrical resistance due to the ageing related to the resistance measured before the plasma treatment.

RESULTS

The narrowest ($4\mu\text{m}$) paths were destructed during the deposition of the protective films, so further studies on the ageing of the passivating layers were limited to the paths of widths $25\mu\text{m}$ and $10\mu\text{m}$. Figures 5 and 6 illustrate the effect of oxygen concentration in mixtures $\text{TMOS} + \text{Ar} + \text{O}_2$, at deposition time of 5 min, on the number of unaffected paths in the structures TT2 TT5/TT6, depending on the time of ageing.

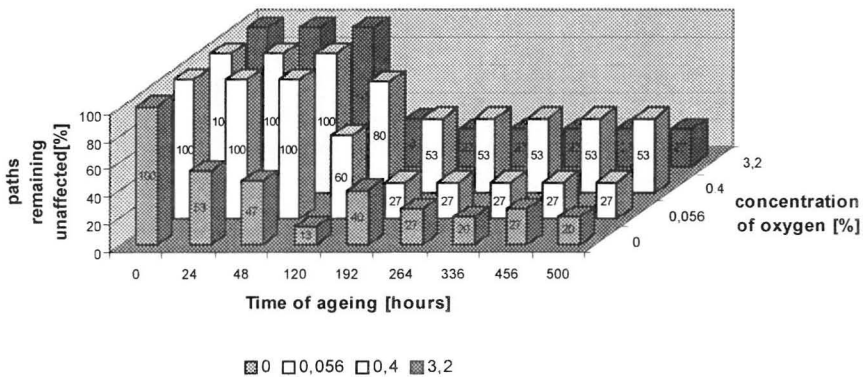


Fig. 5. Effect of ageing time on the number of paths remaining unaffected. Duration of film deposition 5 min. TT2 structure. Path width $25\mu\text{m}$.

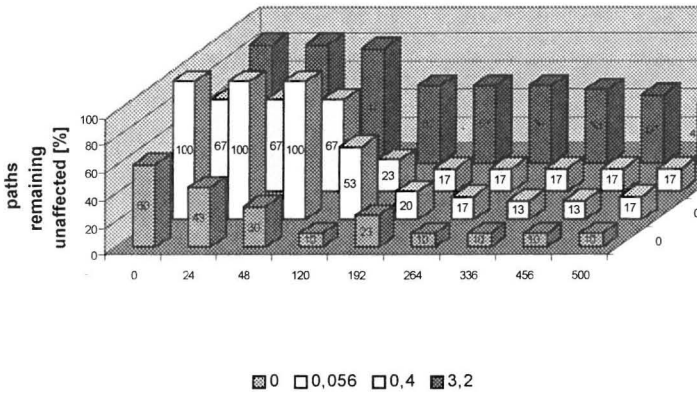


Fig.6. Effect of ageing time on the number of paths remaining unaffected. Film deposition time 3 min. TT5/TT6 structure. Path width 10 μm .

The results presented in Figs. 5 and 6 indicate, that a part of the 25 μm i 10 μm paths have been destroyed, in the ageing test, as a result of reaction with water vapour that penetrated the protective coating and attained the metal surface. The protective ability of the films increase, in general, with increasing concentration of oxygen in argon. Under the most favourable conditions a 500-h ageing test was passed effectively by ca. 60% of 25 μm paths and by 40-50% of 10 μm paths.

Figures 7 represents the effect of ageing time on the number of unaffected paths in different structures, protected with epoxy resin HYSOL FP 4511, used normally for encapsulation of such types of circuits.

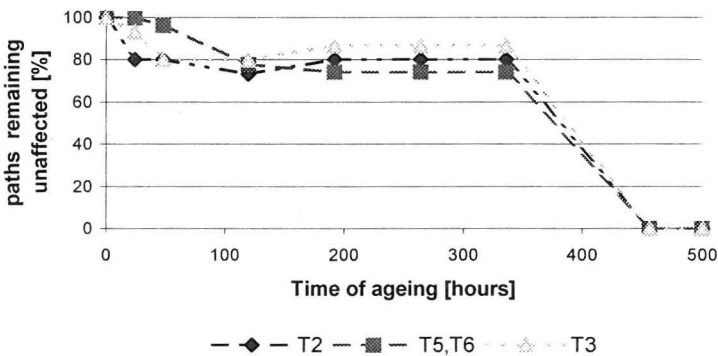


Fig. 7. Effect of ageing time on the number of unaffected paths in different structures protected by epoxy resin HYSOL FP 4511 produced by Dexter.

Figure 8 shows a photograph of TT5 protected with the epoxy resin, which has been destroyed, in part as quickly as in the initial 48 h of the ageing test.

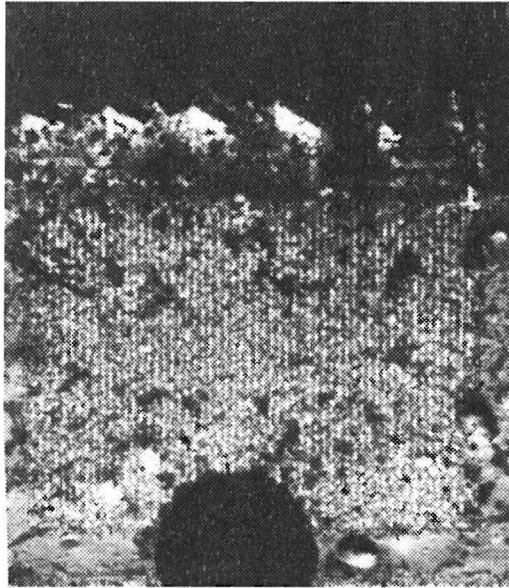


Fig.8. TT5 structure protected by epoxy resin HYSOL FP 4511, after the ageing test.

In the course of the ageing test (alternating heating and cooling) the resin undergoes repeated expansion and shrinkage which, as a result, destroy all joints of the circuits. A rapid growth of electric resistance of the circuits and a decrease of the number of effective circuits are observed in the course of the ageing process (Fig. 9).

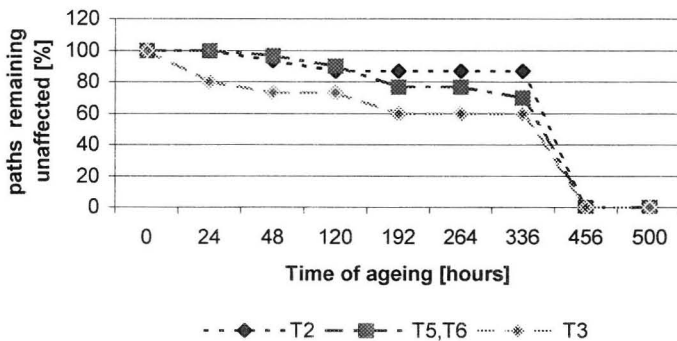


Fig.9. Effect of ageing time of unprotected coatings on the number of TT2, TT3 and TT5/TT6 circuits remained unaffected.

Both the epoxy resin and the aluminium oxide layer formed during the oxidation of aluminium protect the conducting paths from complete destruction for the ageing time not exceeding 336 h. Like in the structures protected with silicoorganic films the number of the paths completely destroyed after a definite time of ageing depends on their width (narrower paths are more readily destroyed than wider ones). Comparing the protective ability of the coating deposited by the PE-CVD method with those of the epoxy resin HYSOL points to the advantage of the former ones. The silicoorganic films deposited under optimum, non-destroying conditions are thinner and more effective in protection of the circuits. This fact has been evidenced by a positive result of a 500-h ageing test. The relation between the number of non-destroyed circuits and the ageing time indicates that the results obtained for the testers protected with the epoxy resin are more reproducible than those protected by the silicoorganic films. No wonder, since this resin has been used for long for the purpose, its properties and its depositing conditions have been carefully optimised, whereas the protective coatings obtained by the CVD are actually in the stage of preliminary testing. Measurements of electrical resistance of survived circuits have shown only small changes in the protected circuits, contrary to unprotected ones, which undergo oxide passivation during the heat treatment.

CONCLUSIONS

Thin silicoorganic films deposited from TMOS at room temperature provide an effective corrosion protection of aluminium circuits on silicon plates providing, that the deposition parameters are carefully selected so that the aluminium paths of the circuits are not damaged during the film deposition.

REFERENCES

1. **Fabianowski W., Jachowicz R., Azgin Z., Sochoń J., Rżanek-Boroch Z., Sentek J., Schmidt-Szałowski K.**, Passivation properties of thin silicon oxide films with operating under atmospheric pressure. Proceedings 14th International Symposium on Plasma Chemistry, Praha, 1999.
2. **Schmidt-Szałowski K., Rżanek-Boroch Z., Sentek J., Rymuza Z., Kusznierevicz Z., Misiak M.**, Thin films deposition from hexamethyldisiloxanen and hexamethyldisilazane under dielectric-barrier discharge (DBD) conditions, *Plasmas and Polymers* Vol.5, nr.3/4, 2000.

POWŁOKI ANTYKOROZYJNE NANOSZONE METODĄ PE-CVD POD CIŚNIENIEM ATMOSFERYCZNYM

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S t r e s z c z e n i e. Przedmiotem badań są powłoki z SiO₂ osadzone pod ciśnieniem atmosferycznym metodą PE-CVD z tetrametoksylanu (TMOS) stosowanego w mieszaninach TMOS + Ar i TMOS + Ar + O₂ w celu zabezpieczenia układów scalonych przed korozją. Powłoki nakłada się na aluminiowe obwody drukowane (testery), poddaje się procesowi starzenia w temperaturze 121°C i wilgotności względnej 100%. Proces ten pozwala na obserwację trwałości powłok natomiast zmiany rezystancji obwodów świadczą o postępie korozji.

S ł o w a k l u c z o w e : cienkie warstwy, warstwa antykorozyjna.