acta phys. slov. 36 (1986), No. 2

INVESTIGATIONS INTO DEPOSIT FORMING DURING ALUMINIUM ETCHING IN CCl_4 PLASMA[1])

V. MARTIŠOVITŠ[2]), J. MIERTUŠOVÁ[2]), V. ŠURDA[2]), J. TRNOVEC[2]), M. ZAHORAN[2]), Bratislava

In the paper deposit forming in Al structures in CCl_4 plasma etching was studied. Deposits were analysed by IR and UV spectroscopy and X-ray microanalysis. Also some possibilities of its removing were investigated. It is more effective to prevent deposit forming during etching by heating the apparatus.

ИССЛЕДОВАНИЕ ОБРАЗОВАНИЯ ОСАДКА НА АЛЮМИНИИ ПРИ ТРАВЛЕНИИ В ПЛАЗМЕ CCl_4

В работе изучено образование осадка на алюминиевых структурах при травлении в плазме CCl_4. Анализ осадков проводился при помощи инфракрасной и ультрафиолетовой спектроскопий, а также посредством рентгеновского микроанализа. Были изучены также возможности удаления этих осадков. Оказалось, что воспрепятствовать образованию осадков наиболее эффективно можно непосредственно в процессе травления.

I. INTRODUCTION

Aluminium can be succesfully etched in chlorinated plasmas, such as CCl_4 BCl_3 and $SiCl_4$ [1—5]. Etching in CCl_4, the most commonly used etching gas, provides selectively and anisotropically etched figures of aluminium under certain conditions. But this technological process is connected with many problems such as end-point detection [6, 7], long and frequently erratic etch initiation times associated with the removal of native aluminium oxide [11], etch inhibiting effects of ambient water vapour, resist degradation and erosion leading to the loss of critical dimensions [8], toxic and corrosive etchants or etch products, and photoresist mask removal when after a typical plasma ashing cycle a residue is formed [8]. All these problems are closely connected with polymerized films deposited during etching where special attention is to be paid to the $AlCl_3$ etch product [9]. $AlCl_3$ is a highly reactive molecule which can cause failure of photoresist, poor selectivity to oxide (SiO_2) and corrosion of the aluminium pattern after the etch [10].

The purpose of the present paper is: 1. to investigate the polymerized films deposited on the inner wall of the reactor and on the etched aluminium surface during an etching process in CCl_4, 2. to study how to prevent the deposition of the films or how to remove the films already deposited.

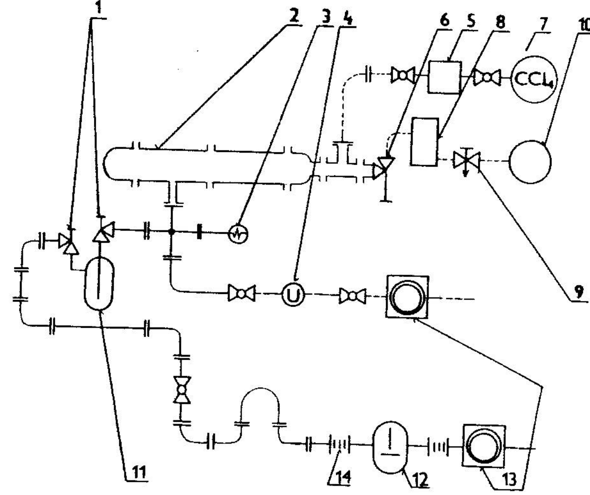

Fig. 1. Scheme of the vacuum apparatus. 1 — vacuum valve, 2 — etching space, 3 — Pirani gauge, 4 — U-tube manometer, 5 — mass flow controller, 6 — needle valve, 7 — CCl_4 tank, 8 — drying reactor, 9 — control valve, 10 — gas tank, 11 — cooled trap, 12 — Roots pump, 13 — rotary oil pump, 14 — bellows.

II. EXPERIMENTAL METHOD

In order to eliminate the catalytic influence of the metal surface an all-glass apparatus was used in the experiment. The vacuum system consisted of commercial Simax glass tubes with normalized flanges. The system was attached to a Roots -type blower, backed by a rotary pump with a standard hydrocarbon oil. The vacuum system can be pumped down to pressures of 10^{-2} Pa or less during 5 min. The etching reactor consisted of a cylindrical Simax glass discharge tube 20 cm long with an internal diameter of 5 cm. A plasma was sustained by a r.f. electrical discharge excited between two external brass electrodes — of a 24 cm^2 area — connected to a r.f. generator of 7 MHz frequency. Fig. 1 illustrates the arrangement of the reactor. The arrangement of the etched sample in the discharge tube is shown in Fig. 1a.

[1]) Contribution presented at the 5th Symposium on Elementary Processes and Chemical Reactions in Low Temperature Plasma, ŠTIAVNICKÉ BANE, May 21—25, 1984.

[2]) Katedra experimentálnej fyziky MFF UK, Mlynská dolina, 842 15 BRATISLAVA, Czechoslovakia.

Such a non-standard reactor and vacuum system were used to eliminate secondary effects at the deposition of polymer films. A great advantage of this arrangement was that the parts with deposited films could be easily removed and replaced by new and clean glass tubes. Also a small amount of deposited film can be easily observed. Naturally, the etching uniformity within the sample was not very high, but on the other hand it has enabled us to observe the etching process with the naked eye.

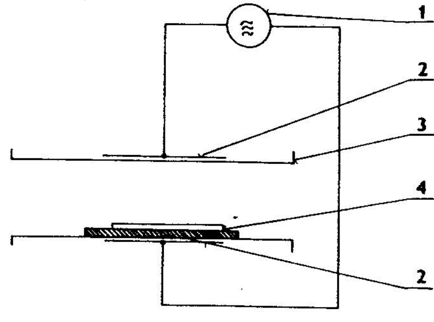

Fig. 1a. The arrangement of the discharge space. 1 — r.f. generator, 2 — external brass electrodes, 3 — Simax glass tube, 4 — elox holder with etched sample.

Liquid CCl_4 of chemically pure grade additionally purified in vacuum was used as a source of the CCl_4 vapour. The CCl_4 vapour entered the reactor through a Tylan mass flow controller. The vapour pressure was indicated by a Pirani gauge which was periodically calibrated by an oil U-tube manometer. The CCl_4 vapour and the etch products were removed by a liquid nitrogen cooled glass trap. The leak from the atmosphere did not exceed 10^{-6} Pam^3 s^{-1}.

The etching process was monitored by measuring the r.f. peak voltage across the external electrodes. The r.f. power was not measured because the values obtained could not be compared with results corresponding to standard planar reactor systems due to the difference in geometry. Therefore, the conditions were estimated by measuring the aluminium etch rate.

III. RESULTS AND DISCUSSION

As a first step, the polymerized films deposited in the absence of the etched sample were studied. The working pressure of CCl_4 vapours and r.f. voltage on the electrodes were variable parameters.

The velocity of deposits forming and their amount is increasing with the increase of the CCl_4 vapour pressure in the range 10—60 Pa at a constant r.f. voltage on the electrodes. At working pressure 60 Pa the discharge tube was covered by the non-transparent deposit for a few minutes.

At constant working pressure 40 Pa the colour of the deposit changed rapidly with the increasing r.f. voltage on the electrodes in the range 400—800 V. At a voltage over 600 V the deposit had a yelow-brown colour and it was more difficult to remove it than the white powder formed at the lower voltage.

The analysis of the deposit composition was made by absorption IR spectroscopy. The deposit was mechanically removed from the discharge tube walls and KBr discs were formed. In the spectrum -curve I in Fig. 2- the H_2O peak is clearly

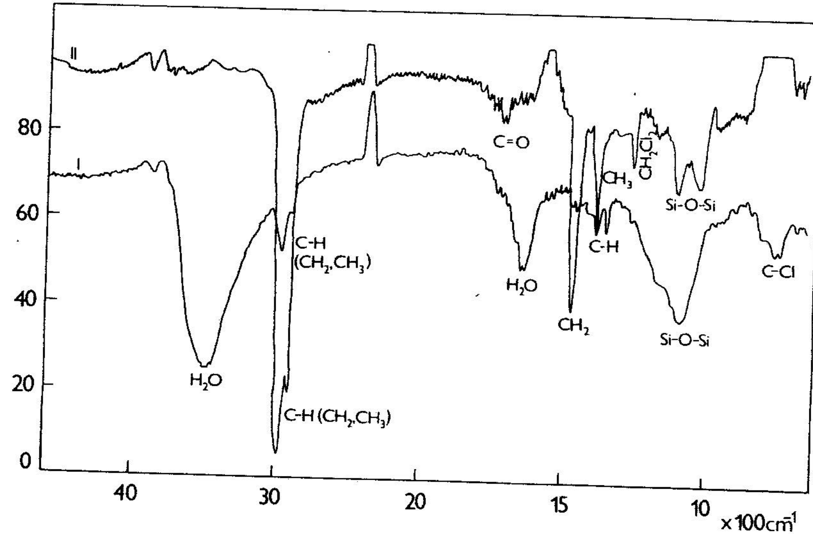

Fig. 2. IR spectra of deposit. I — KBr disc, II — solution in CCl_4.

seen, which can be caused by hygroscopics KBr and other products of etching. There are also CH_2 and CH_3 groups and peaks of C—Cl and Si—O—Si bonds. One part of the deposit sample was dissolved in CCl_4 and the IR spectrum was measured -curve II in Fig. 2. In this spectrum peaks of C—H valence vibrations, $SiCH_3$, CH_2Cl_2, $CHCl_3$ deformation vibrations and C—O admixtures can be observed.

From the detailed analysis of IR spectra it is seen that CCl_4 is split in the discharge. The deposits are oligomers even polymers and the walls of the discharge tube are slightly damaged. An analysis of UV spectra confirmed the dimer even polymer structures in the deposit. These spectra were measured on flint glass samples placed in the discharge space and behind it.

After obtaining information about the deposit forming in the CCl_4 discharge the aluminium samples (of a 4 cm^2 area) were placed into the discharge space. The quality of the Al surface etching was controlled by X-ray microanalysis. The etching at low working pressure of CCl_4 (under 20 Pa) can be characterized as very

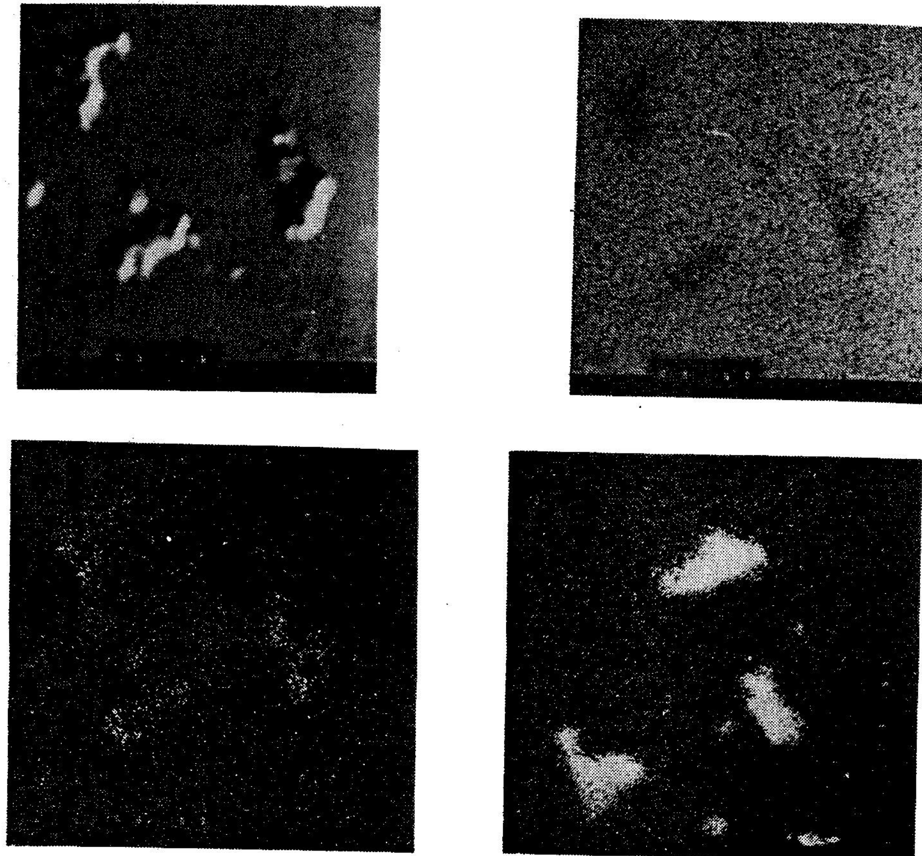

Fig. 3. Photos of RTG analyser JEOL (1 cm = 33 μ). a) 349 — composition of surface, b) 350 — Si signal, c) 351 — Al signal, d) 352 — Cl signal.

inhomogeneous. The photos in Fig. 3 were made by microanalyser JEOL from the sample etched at a pressure 12 Pa and a 500 V r.f. voltage. From these photos can be seen that Al and Cl were detected simultaneously (white places in the photos). It means that the etching was obstructed with an Al and Cl compound — probably $AlCl_3$.

The etching above 20 Pa working pressure was more homogeneous. The X-ray analysis did not detect signals from Al and Cl. The whole surface reflected only one signal of Si. C and O were detected below noise level.

During etching at working pressures above 40 Pa the deposit forming was dominant and prevailed over the etching.

Series of experiments were made to remove deposit films. In the discharge space of the reactor contamined with etching products the intensive r.f. discharge at pressures from 1 Pa to 10^2 Pa in different gases was applied. In these experiments we did not succeed to remove deposit films either in the Ar plasma (bombardement with energetical ions) or in O_2, H_2, CH_4 and H_2O plasma reactions of particles formed in plasma with a deposit. Changes in the composition of deposit films were not observed either.

The prevention of deposit forming on the walls of the discharge tube during etching was the most effective. The vapour pressure of $AlCl_3$, C_2Cl_6 and other products of etching strongly depend on temperature. The saturation vapour pressure of $AlCl_3$ is $\approx 10^{-1}$ Pa at room temperature. It causes a small volatility of $AlCl_3$. The vapour pressure of $AlCl_3$ increases with increasing temperature and at 100 °C is 133 Pa [12]. At this temperature $AlCl_3$ does not condensate on the surface and can be pumped out.

The deposition on the inside walls of the reactor was not observed when the temperature of the discharge tube walls increased to 80 °C. The reproducibility and quality of the etching were much higher in the heated apparatus than in the apparatus without heating.

REFERENCES

[1] Schaible, P. M., Metzger, W. C., Anderson, J. P.: J. Vac. Sci. Technol. *15* (1978), 334.
[2] Curtis, B. J., Brunner, H. J.: J. Electrochem. Soc. *125* (1978), 829.
[3] Ukai, K., Hanazawa, K.: J. Vac. Sci. Technol. *16* (1979), 385.
[4] Sato, M., Nakamura, H.: J. Vac. Sci. Technol. *20* (1982), 186.
[5] Saia, R. J., Gorovitz, B.: Solid State Technol. *26* (1983), 247.
[6] Curtis, B. J.: Solid State Technol. *23* (1980), 129.
[7] Park, K. O., Rock, F. C.: J. Electrochem. Soc. *131* (1984), 214.
[8] Tracy, C. J., Mattox, R.: Solid State Technol. *25* (1982), 83.
[9] Bernacki, S. E., Kosicki, B. B.: J. Electrochem. Soc. *13 L* (1984), 1926.
[10] Spencer, J. E.: Solid State Technol. *27* (1984), 203.
[11] Hiribe, K., Kureiski, K., Tsuchimoto, T.: J. Electrochem. Soc. *128* (1981), 2686.
[12] Rabinovich, V. A., Chavin, Z. J.: *Kratkij chim. sprav.*, Chimija, Leningrad 1978.

Received June 8th, 1984
Revised version received January 24th, 1985