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PLASMA ETCHING OF SILICON AND ITS COMPOUNDS IN THE FREON PLASMA*

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Results applicable to microelectronics technology — showing the interesting behaviour of CF_4+Ar and CHF_3+O_2 mixtures in plasma etching of Si and its compounds in an inductively coupled rf generator in cylindrical quartz chamber in CF_4, CCl_2F_2, CHF_3 gases and some of their mixtures with O_2, N_2, He, Ar suitable for microelectronics technology are presented in this paper.

ПЛАЗМОХИМИЧЕСКОЕ ТРАВЛЕНИЕ КРЕМНИЯ И ЕГО ХИМИЧЕСКИХ СОЕДИНЕНИЙ ВО ФРЕОНОВОЙ ПЛАЗМЕ

В статье приводятся результаты исследований, которые можно использовать в технологиях, применяемых в микроэлектронике. Продемонстрировано интересное поведение смесей CF_4+Ar и CHF_3+O_2 при плазмохимическом травлении кремния и его химических соединений с использованием индуктивно возбуждённой плазмы в цилиндрическом кремниевом реакторе с содержанием газов CF_4, CCl_2F_2, CHF_3 и некоторых их смесей с O_2, N_2, He и Ar.

I. INTRODUCTION

Recent trends in the semiconductor device development and manufacture of Large Scale Integrated circuits (LSI) with higher packing density, expecially advanced very Large Scale Integrated circuits (V-LSI) are impossible without replacing the etching processes in the liquid phase by processes proceeding on the phase boundary gas-solid material, like, e.g. rank utilization of the interaction of plasma with convenient solids. However, processes of the plasma etching, which are mostly unknown, complicate the interpretation of experimental results. In view of the fact a semiempirical investigation is necessary first of all of the possibilities of the plasma etching which may be significantly influenced by changing the plasma marco- and microparameters.

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II. EXPERIMENTAL ARRANGEMENT

Plasma etching in the freon plasma was performed in an inductively coupled plasma device (13.56 MHz, 300 W) equipped by quartz cylindrical chamber of the dimensions of 0.20 × 0.20 m and a uniform spatial inlet of the etching gases. The chamber was evacuated before every experiment for 2 minutes by a rotary vacuum pump to the pressure 10 Pa. The pressure was measured before the distribution of gases into the homogenization jets by a thermocouple vacuum gauge, the flow rate was controlled by a needle valve with a rotameter. In our experiments was also used perforated Al-cylinder (etching tunnel) with dimensions of 0.12 × 0.20 m. The samples of SiO_2 were prepared by thermal oxidation of Si, those of Si_3N_4 by a high temperature CVD process (1000 °C) and those of SiO_2 +.5 % P by CVD technology. The Si substrates were of the N-type, [111] orientation. A Lachema negative photoresist SCR — 3.3 was used for masking the samples. Not purified gases were used before the inlet to the reagent chamber with respect to the low purity of environment. The gases were mixed at a convenient distance before being introduced into the chamber in order to prevent their inhomogeneous distribution. Etched profiles were measured by a Talystep or interferometer. The reproducibility of the measurements was about ±5 %. The activation of surfaces by 0_2 plasma was performed before applying the plasma etching. To achieve better results inductive heating of certain samples in N_2 and Ar gases was carried out. The results presented in this paper were obtained on one and a half inches substrates with the rear side covered by a photoresist placed in the centre of the chamber.

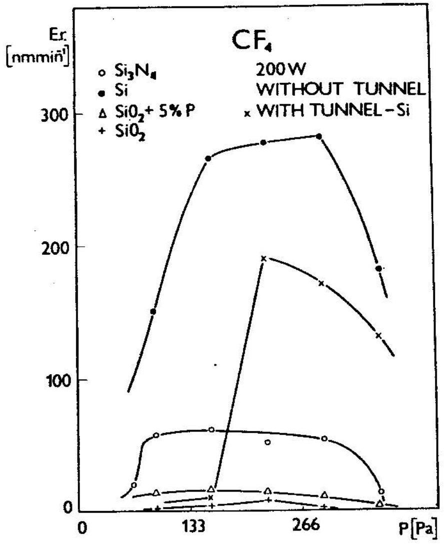

Fig. 1. Variation of etch rates with pressure in CF_4 gas.

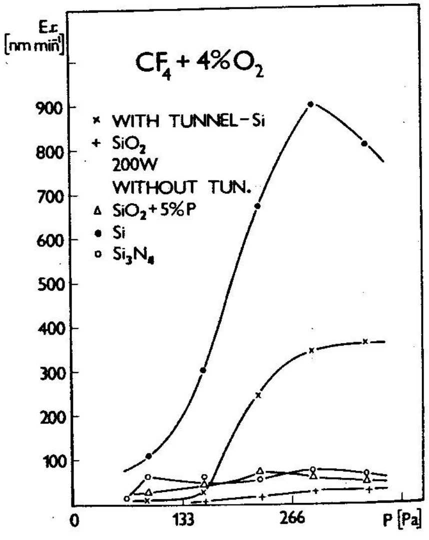

Fig. 2. Variation of etch rates with pressure in $CF_4 + O_2$ mixture.

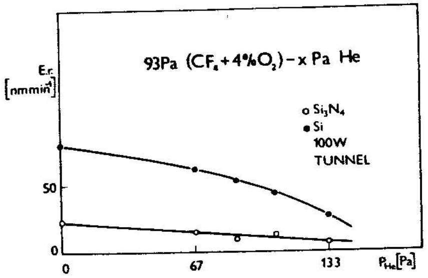

Fig. 3. Variation of etch rates with pressure in $CF_4 + O_2 + He$ mixture.

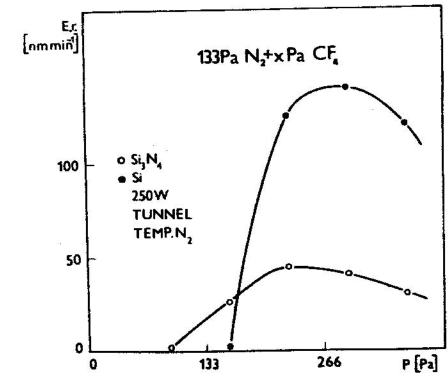

Fig. 4. Variation of etch rates with pressure in $CF_4 + N_2$ mixture.

III. RESULTS

According to literature, CF_4 plasma is most frequently used for plasma etching of silicon and its compounds [1—5]. Our results obtained in these experiments are described in Fig. 1. Molecular oxygen was added to the CF_4 gas to obtain a higher concentration of the atomic fluorine and reduce its recombination, which is of great importance in the plasma etching of silicon — see Fig. 2. The behaviour of the mixtures $CF_4 + O_2 + He$, $CF_4 + N_2$ and $CF_4 + Ar$ with respect to the possibility of influencing the plasma properties by inert gases has been also studied — see Figs. 3, 4, 5.

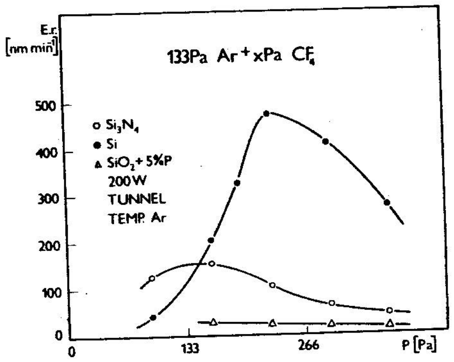

Fig. 5. Variation of etch rates with pressure in CF_4 + Ar mixture.

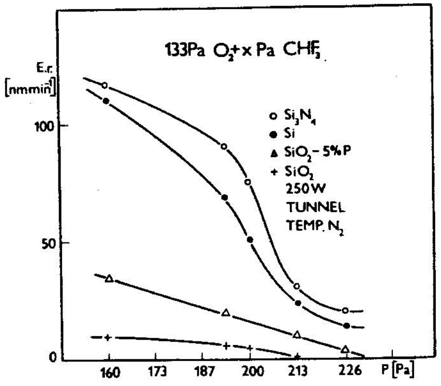

Fig. 6. Variation of etch rates with pressure in $CF_3 + O_2$ mixture.

Among other gases CCl_2F_2 was examined, unfortunately in the used type of apparatus this gas behaved impassively with respect to silicon and all its compounds in the range of pressures 60—300 Pa, generator power 50—300 W, with and without the presence of an Al-cylinder. Even its mixtures with He, N_2 and O_2 were not reactive. Similarly negative results were obtained with the CHF_3 gas. However, during the investigation of the $CHF_3 + O_2$ mixture the reaction with silicon and its compounds did not start at room temperature, only an increase of the temperature of substrates to 150—200 °C initiated the reaction. The results obtained under these conditions are shown in Fig. 6. Three kinds of inductive heating of samples were used: a) no heating — CF_4, $CF_4 + O_2$, $CF_4 + O_2 + He$, CHF_3, CCl_2F_2, $CCl_2F_2 + He$ plasma; b) heating in $N_2 - CF_4 + N_2$, $CHF_3 + O_2$, CCl_2F_2, $CCl_2F_2 + O_2$ plasma; c) heating in Ar — $CF_4 + Ar$ plasma.

The heating was performed for about 5 minutes, at a generator power of about 300 W and a pressure 500—600 Pa.

IV. DISCUSSION

The results obtained in CF_4 plasma are in good agreement with those of formerly published articles. The etching of silicon in CF_4 plasma is effected chiefly by atomic fluorine while silicon compounds, on the other hand, are etched by CF_x radicals and other fragments of molecules of CF_4, as evidenced by the results of many papers dealing with elementary processes in CF_4 plasma [4, 7—12].

With respect to the theory of the elementary processes in plasma we can explain the experimental data shown in Figs. 1—6 as results of an increased or decreased generation rate of the etching components, their recombination properties in the volume of plasma as well as on the surrounding surfaces including the surface of the etched material. The properties of plasma are also changed by the physical-chemical reactions on the surfaces of samples and by the desorption of the reaction products. With respect to the complication of the problems of plasma etching the changes of the etching rates of materials consequently do not correspond only to changes of the plasma behaviour. The extreme behaviour of some plasma parameters could have significant influence on the etching rates, the selectivity and the etched profiles. To ensure the applicability of plasma etching in the IC technology production it would be necessary to pay great attention to problems of elementary processes in the freon plasma. The great importance of surface reactions and their changes, caused by the temperature of the etched material is evidenced by the behaviour of the $CHF_3 + O_2$ plasma, where etching starts at substrates temperatures of 150—200 °C. Negative results obtained with the CCl_2F_2 and CHF_3 plasma can be explained by lower values of the binding energy of atomic chlorine with the rest of the molecule than the values of the binding energy of fluorine [13]. Then freon plasma contains mainly atomic chlorine, which is inert to silicon and its compounds. The results presented here are convenient for using in the IC manufacture technology. It is rather difficult to find the possibility of applying the above mentioned methods because of the influence of other parameters, as the photomask lifetime, the accumulation of charge from the plasma in the dielectrics, the undercutting of the mask, the slopes of the steps, etc.

V. CONCLUSIONS

Some results obtained in experiments with the plasma etching of silicon and its compounds were summarized in this paper. Some complications connected with a more exact solution of these problems were also discussed. The selectivity of plasma etching of silicon and its compounds, its reproducibility, simplicity and rate show the advantage of the replacement of wet chemical etching by plasma etching for the purposes of IC manufacture technology.

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