CF4 AND CBRF3 PLASMA ETCHING INDUCED MODIFICATION OF SILICON NEAR SURFACE LAYERS

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ABSTRACT

Deactivation of boron atoms and formation of deep levels in the band gap of Si etched in CF_4 plasma were observed and comparatively studied by C-U and DLTS methods. The two phenomena depend differently on etching conditions and appear to be not interrelated. $CBrF_3$ plasma etching induces different deep defect states that are more localized near the etched surface.

INTRODUCTION

Deactivation of boron in p-Si after dry etching was observed by many authors /1-5/ and explained in terms of hydrogen incorporation in Si lattice. At the same time plasma or reactive ion etching may produce considerable lattice damage introducing deep defect states in the band gap of Si /5-8/ which in principle may as well contribute to dopant compensation mechanism. The aim of this study was to make more clear the relative role of this latter mechanism under different etching conditions.

EXPERIMENTAL

Wafers of boron-doped (100) Cz Si of resistivity 10 Ω cm were etched in diode type reactor operating at 75 kHz. Two gases CF_4 and $CBrF_3$ were used. Discharge power was 100 W, the a.c. voltage being 400 V. The pressure in the reactor varied from 15 to 50 Pa. Calculations show that 64% of ions have energy less than 30 eV at pressure 30Pa /9/. Wafers were placed on the cathode, whose temperature was kept 35^{o}C. Etch duration was 5 min. After etching the wafers were cleaned in $HF:H_2O$ (1:4), $H_2SO_4:H_2O_2$ and $NH_4OH:H_2O$. Cleaned wafers were annealed in nitrogen at 300, 350, 450 and

$600^{o}C$ for 10 or 15 min. Al or Mg Shottky contacts were fabricated by thermal sputtering in vacuum 10^{-3} Pa and were used for capacitance-voltage and DLTS measurements. Small signal DLTS was used for depth profilling /10/.

RESULTS AND DISCUSSION

Fig.1 shows typical capacitance-voltage characteristics for the Shottky diodes, formed on Si after plasma etching in CF_4 at different pressures in the chamber. Corresponding concentrations of the deactivated atoms of boron versus depth are plotted in fig.2. The curves were found to be temperature independent in the temperature range down to 77K. No hysteresis of the C^{-2} versus U dependences was detected that could indicate that some deep defect states may be involved. At fig.3 DLTS spectrum typical for Si etched in CF_4 is presented. The temperature of the peak maximum is 196K for the frequency of the refilling pulses F=70 Hz (hole

Fig.1

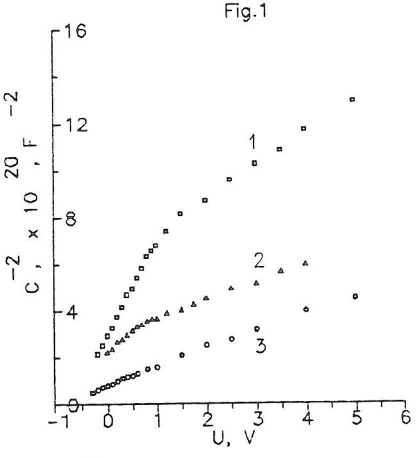

Fig.2

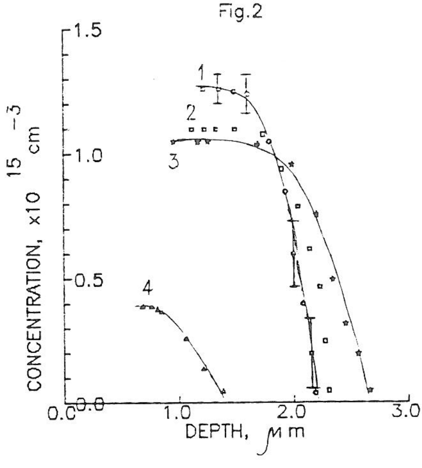

Fig.1. C-U plots for Shottky diodes formed on Si, etched in CF_4: 1 - at 30 Pa; 2 - at 50 Pa; 3 - at 20 Pa and annealed at $350^{o}C$ for 10 min.

Fig.2. Depth dependence of concentrations of deactivated boron atoms after etching in CF_4: 1 - at 20 Pa; 2 - at 30 Pa; 3 - at 50 Pa; 4 - at 20 Pa and annealing at $350^{o}C$ for 10 min.

Fig.3

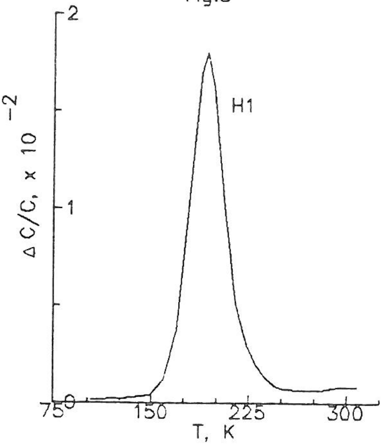

Fig.4

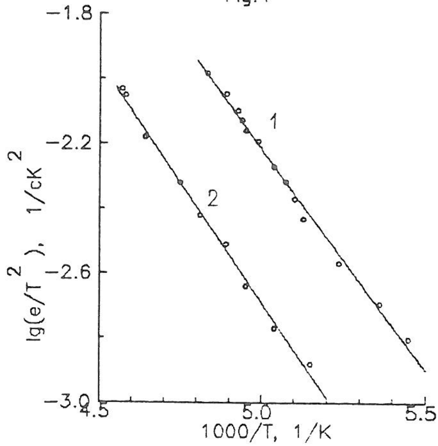

Fig.3. DLTS spectrum of Si, etched in CF_4 at pressure 20Pa. Emission rate of holes $e=1.65x10^2c^{-1}$; $U_b=U_p=1V$.

Fig.4. Arrhenius plots for DLTS peaks: 1 - H1, observed in CF_4 etched Si; 2 - H2, observed in $CBrF_3$ etched Si.

emission rate $e=1.65*10^2c^{-1}$). The Arrhenius plot for this DLTS peak is presented in fig.4(1), which gives energy level of the centers E=0.27 eV above the valence band and the value of cross section $2x10^{-17}cm^2$. These defects were found to anneal out already at 300^oC. The profiles of concentrations of the H1 centers are shown in fig.5 for three different pressures in the reactor: 20, 30 and 50 Pa. As it is seen from the figure, strong dependence of the concentration of the H1 centers on pressure and hence the energy of the ions takes place whereas the concentrations of deactivated boron atoms are almost pressure independent (fig.2). It is also seen from fig.5 and fig.2 that the concentrations of deactivated boron atoms and the concentrations of deep centers may be comparable for pressure 20 Pa only in the range of depthes $< 1\,\mu m$ and are practically incomparable for pressures 30 and 50 Pa.

Fig.5

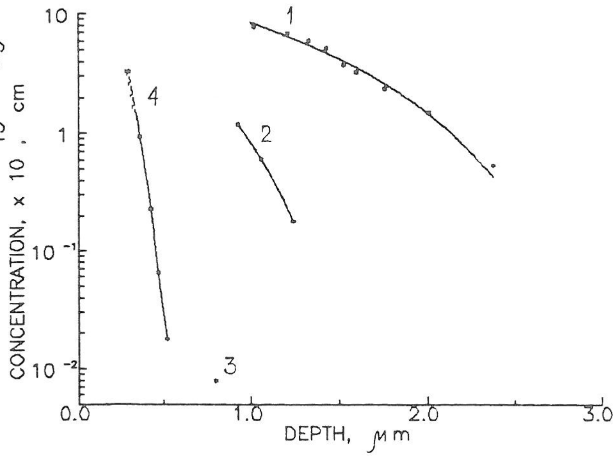

Fig.5. Depth profiles plot for deep centers in plasma etched Si: 1 - 3 - for H1 centers in Si etched in CF_4 at pressure 20, 30 and 50 Pa, correspondingly; 4 - for H2 centers in Si etched in $CBrF_3$ at pressure 30 Pa.

Fig.6

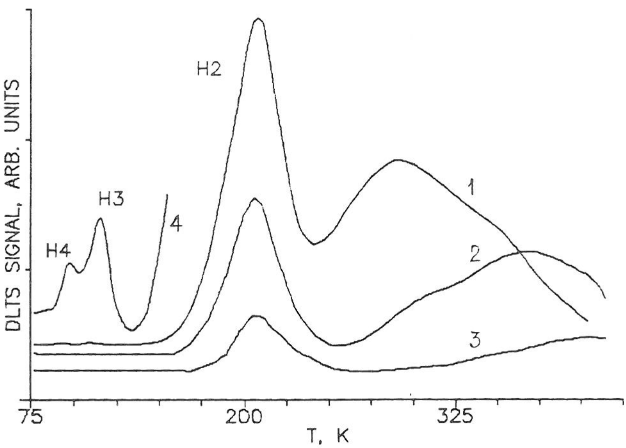

Fig.6. DLTS spectra in $CBrF_3$ plasma etched Si. $e=1.65x10^2c^{-1}$; U_p=0.3 V; 1 - U_b=0 V; 2 - U_b=0.2 V; 3 - U_b=0.3 V; 4 - same as 1, x 30.

Thus from all experimental results described above it is clear that deep states of defects, produced near Si surface during plasma etching are not responsible for dopant deactivation mechanism, despite the fact that the depth where deep levels are still observed may sometimes also reach several μm (fig.5).So we suppose that incorporation of hydrogen was in fact the reason for boron deactivation observed in CF_4 plasma etched Si.

Plasma etching in $CBrF_3$ led to somewhat different results in comperison with CF_4 plasma etching regarding both the dopant deactivation effect and generation of deep states in the band gap. First, the effect of deactivation of boron in $CBrF_3$ plasma etched Si was very small if observed at all. This fact is not simple to explain unambiguously since all the other parameters of plasma etching were identical and both gases used contain no hydrogen. However, estimates show that the effective flux of protons needed to ensure the effect of dopant deactivation presented in fig.2, is about $10^9 cm^{-2} c^{-1}$, which gives the effective concentration of protons $10^4 cm^{-3}$ or the effective pressure of hydrogen 10^{-11}Pa, which is far beyond the controllable limits.

At Fi.6 typical DLTS spectra in $CBrF_3$ etched Si are presented. The most prominent DLTS peak H2 corresponds to the energy level of the defects E=0.29 eV the cross section being $1.9x10^{-17} cm^2$. The peak temperature is now 208 K for F=70 Hz. The Arrhenius plot for the H2 centers is shown at fig 4(2). The depth profile for the H2 centers is shown at fig.5(4) for etching at 30 Pa. It is seen that the H2 centers are practically localized in about 1 μm deep near surface layer. Plasma etching induced surface states are also seen on the DLTS spectra as broad peaks that vary with applied bias (see fig.6) The experiments with annealing showed that the H2 centers disappear after annealing at 300^{o}C, whereas surface states peaks behave differently. They remain practically unchanged after annealing at 350^{o}C, decrease strongly after annealing at 450^{o}C and were found to begin to grow again after annealing at 600^{o}C

The concentrations of H3 and H4 centers, which are observed at higher amplification (spectrum 4 at fig.6) are less than that of H1 centers by more than two orders. These centers are annealed at 300^{o}C as well and their concentrations decrease rapidly with depth alike the concentration of the H2 centers. We found for the H3 centers: $E=E_V+(0.19-0.20)$eV; $\sigma=(2-9)x10^{-16} cm^2$. For the H4 centers : $E=E_V+(0.12\pm0.01)$eV; $\sigma \approx 1x10^{17} cm^2$. The H3 centers resemble very much divacancy in silicon /11/ ($E=E_V+0.21eV$; $\sigma = 2x10^{-16}cm^2$).

The exact nature of the H1 and H2 defects induced by CF_4 or $CBrF_3$ plasma etching is not yet clear. It is reasonable to suppose that these defects are different kinds of vacancy complexes. However, it is not likely that mere chemical formulas of the etchant gases directly determine the structure of these complexes. Different authors sometimes report different data concerning deep levels induced by plasma etching although they use the same etchant gases and similar etching conditions. For example, in /8/ energy level $E_V+0.26$ eV was observed in p-Si after reactive ion etching in SF_6 (with cross section essentially differing from that of H1 centers observed in this study) and in /3/ two levels 0.36eV and 0.51eV were reported for the same etching conditions. Thus contaminants may also be involved in the defect structure.

The fact that $CBrF_3$ plasma etching induced defects are less penetrative in comparison with that induced by CF_4 plasma etching may be explained by some protective role of Br atoms, which cover the etching surface favoring anisotropic etching.

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