REDUCTION OF $SiCl_4$ TO Si AS A FUNCTION OF FREQUENCY IN LOW PRESSURE RF PLASMAS.

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ABSTRACT

The efficiency of reduction of silicon tetrachloride and the rate of deposition of Si in a low pressure rf plasma was investigated at two frequencies (0.4 and 27 MHz) as a function of position with regard to the rf coil, pressure and time of deposition. At 27 MHz the decomposition efficiency of silicon tetrachloride and the deposition rate of Si are about 3 times higher than at 0.4 MHz.

1. INTRODUCTION

The deposition of Si films from silicon tetrachloride for photo voltaic conversion of solar energy, was investigated due to the lower price of the starting material. The use of Si for solar cells require a minimum concentration of Cl in the Si film. In order to avoid possible interaction between deposited films and substrates,the deposition should be performed at a relatively low substrate temperature. Both purposes may be achieved by employing low pressure RF plasma for the reduction of silicon tetrachloride and deposition of Si. The efficiency of decomposition of the starting material and the rate of deposition of the film in the cold plasma process are strongly dependent on parameters, such as position in the reactor,(with regard to the rf coil), total gas pressure and composition of the gas mixture(1,2). Deposition of Si from silicon tetrachloride has been reported (3) without indicating the dependency on the above parameters.

The efficiency of polymerization or etching in the cold plasma has been found to be dependent on the frequency of the electromagnetic field (4,5). In the present work the effect of two radio frequencies , 0.4 and 27 MHz, on the reduction of silicon tetrachloride and deposition of Si was investigated.

2. EXPERIMENTAL

The Si coatings were deposited from a gas mixture of argon, hydrogen and silicon tetrachloride in an experimental set up described elsewhere (6). The plasma was initiated in a quartz reactor inductively coupled to either an Hyforce 20 rf generator of 0.4 MHz or a Plasma Therm rf generator of 27.12 MHz. The gas mixture contained 2,5% silicon tetrachloride and 7.5%

hydrogen in the argon carrier at pressures between 2 - 10 mbar. The total flow rate of the gas mixture was 125 sccm.

The deposition was performed on substrates of ATJ graphite polished down to 3200 grit alumina and ultrasonically cleaned in ethanol. Before deposition of Si the substrates were treated in a pure argon plasma for 15 minutes. During deposition the bulk temperature of the substrate was about 400°C.

The thicknesses of the deposited coatings, d, were determined by scanning electron microscopy of the fractured coating, while EDAX attachment was employed to determine the relative concentration of chlorine in the Si coating (cCl). The electron energy, Te, and density, ne, were measured in the plasmas at the two radio frequencies by double floating probes and Stark broadening.

3. RESULTS AND DISCUSSION

The electron temperature, Te, was found to be about 3eV at 2.6 mbar, almost independent on the frequency of the electromagnetic field. The electron density, ne, was found to increase with increasing frequency from $9,10^{10}cm^{-3}$ at 0.4 MHz to $5.10^{11}cm^{-3}$ at 27 MHz. These results indicate an increase in the degree of ionization, i.e. higher ion-molecule reactivity at the higher frequency. As a result a higher decomposition efficiency of silicon tetrachloride and higher rate of deposition of Si should be expected.

Figure 1 shows the thickness of the Si films, d, and cCl after 1 hour of deposition, as a function of position of the substrate in the reactor. At both frequencies, the highest rate of deposition was obtained inside the rf coil. The ratio "rd = thickness obtained at 27 MHz/thickness obtained at 0.4 MHz", was found to be about 3. The chlorine concentration in the Si films was almost independent on position inside the rf coil. The ratio "rCl = cCl at 27 MHz/cCl at 0.4 MHz" was about 0.25 inside the coil.

Figure 2 shows the dependence of d and cCl with total pressure in the reactor. d shows a maximum at 2 mbar at both radio frequencies. cCl decreases slightly with increasing pressure at 0.4 MHz and is almost independent with pressure at 27 MHz. At 2 mbar, rd=3 and rCl = 0.3. The values of rCl indicate that at 27 MHz the efficiency of reduction of silicon tetrachloride is about 3 times higher than at 0.4 MHz. Accordingly, the rate of deposition of Si increases about 3 times at 27 MHz as indicated by the values of rd. These results and the increase of ne at 27 MHz indicate that the decomposition of silicon tetrachloride is mainly controlled by ion-molecule reactions.

Figure 3 shows the dependence with time of d and cCl at the two frequencies. It can be seen - Fig.3A - that at values of d smaller than 7 μm the rate of deposition changes with deposition time while at higher values of d the rate of deposition is constant. This indicates that at the initial stages the

substrates affect the deposition. With increasing coating thickness the influence of the substrate diminishes until its influence is cancelled and the rate of deposition is affected by the deposit itself. A constant rate of deposition is reached. Figure 3B shows that cCl decreases with time at both radio frequencies. As shown in Figure 3, rd= 3 - 4 and rCl = 0.25 - 0.30 for all deposition times, indicating again the higher efficiency of deposition of Si from silicon tetrachloride at 27 MHz.

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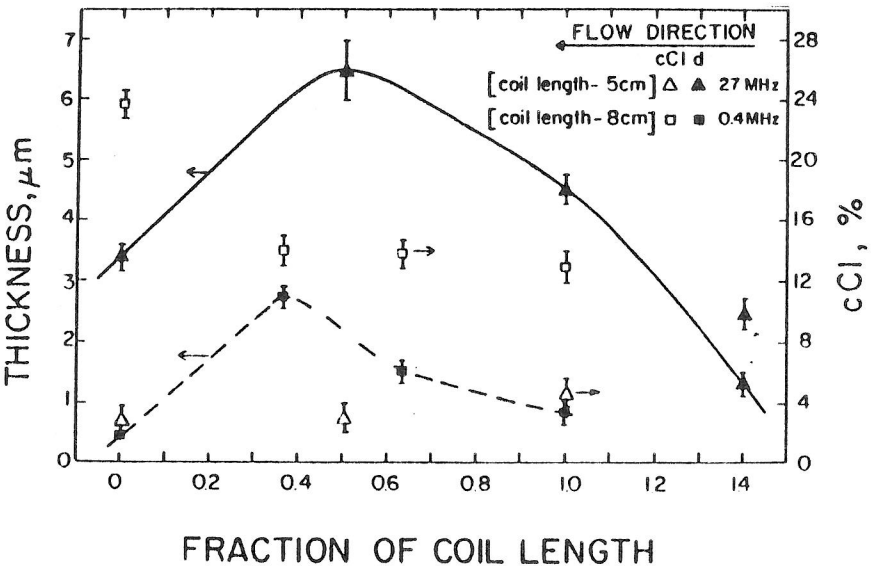

Figure 1. Thickness and chlorine concentration vs. position.
t = 1 hour, p = 2 mbar

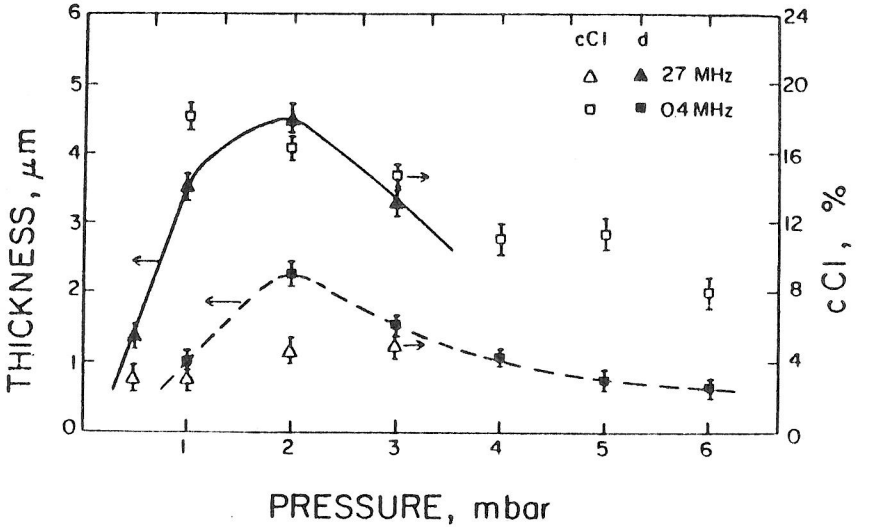

Figure 2. Thickness and chlorine concentration vs. pressure.
position = at the beginning of the rf coil, t=1 hour.

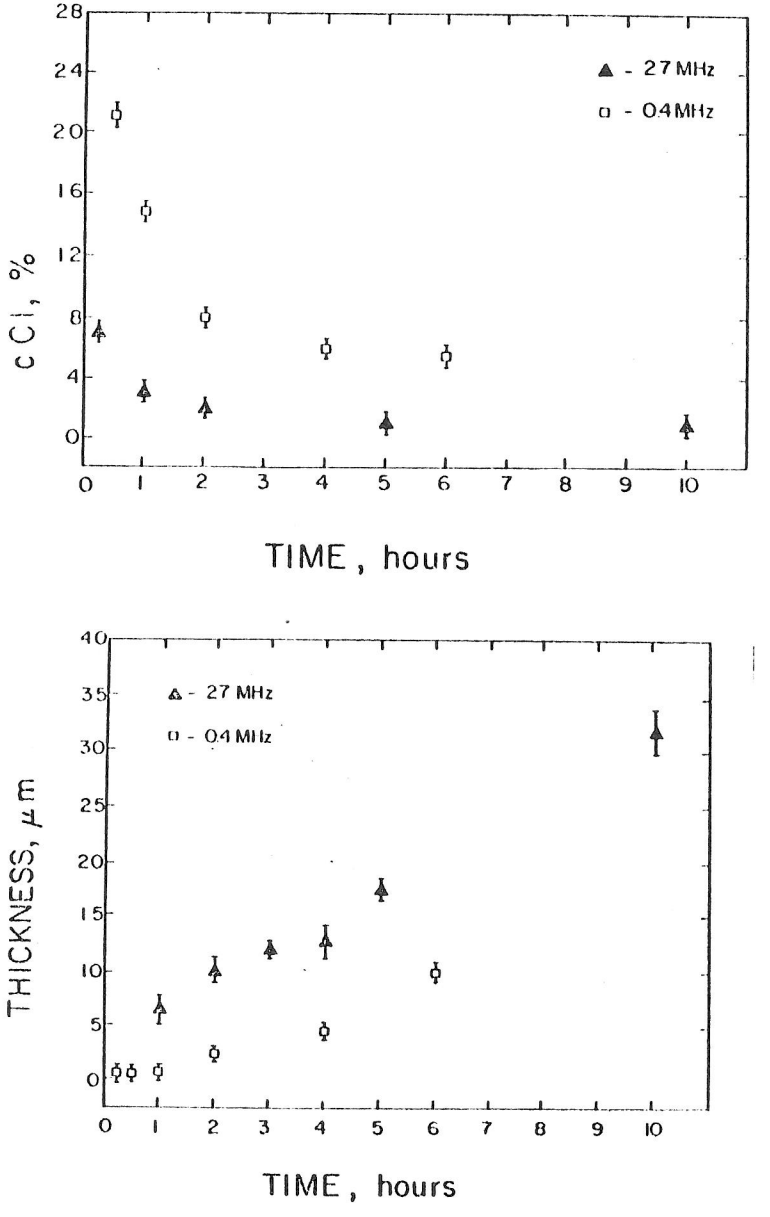

Figure 3. Thickness and chlorine concentration vs. time. position = inside the rf coil, p = 2 mbar.

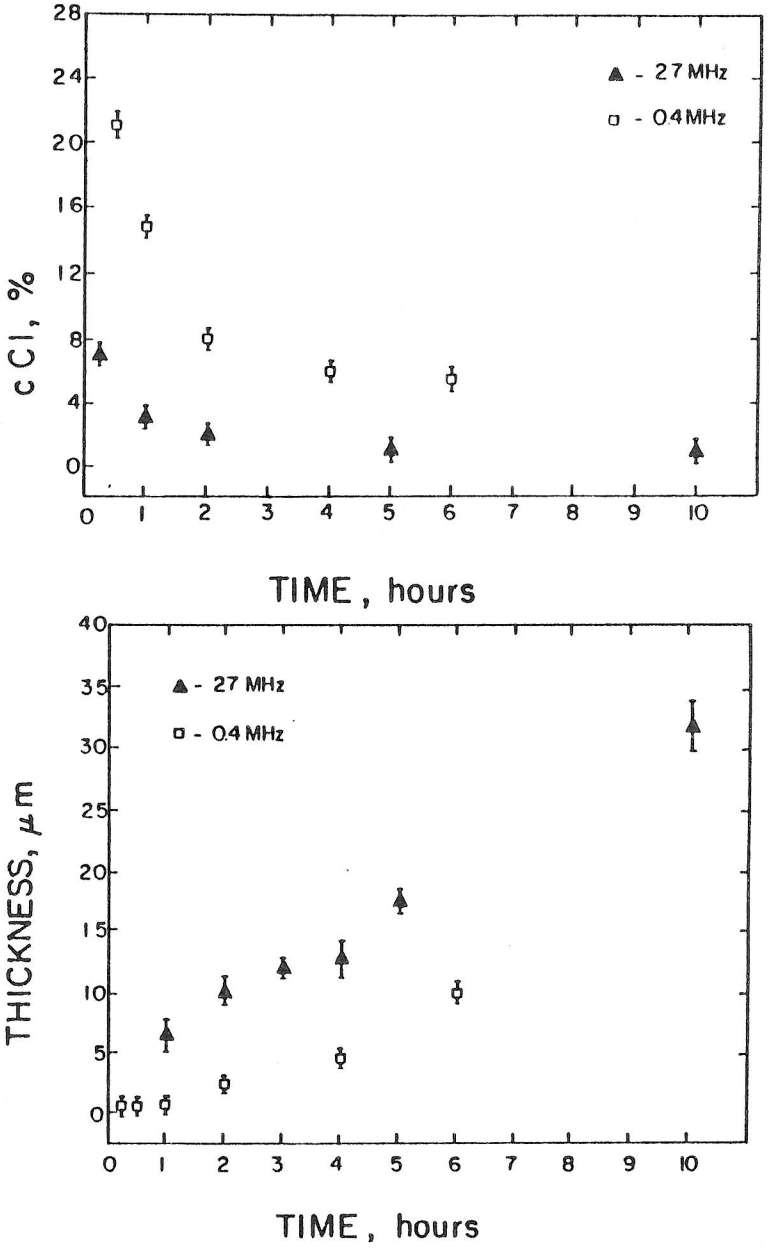

Figure 3. Thickness and chlorine concentration vs. time position = inside the rf coil, p = 2 mbar.