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TDS measurement for low-k porous silica films incorporated with ethylene groups

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1. Introduction

Introduction of the low-*k* film into the ULSI process is very effective in solving propagation delay. Thus, the many low-*k* films have been proposed for the several materials and preparation methods. The spin-on technique is suitable method for low-*k* silica film. This is because it is easy to introduce porogen into the film, which is desorbed during film cure, and these introduced pores work effectively to reduce the *k*-value. Since high porosity is required in order to obtain a lower *k*-value, this requirement leads to serious disadvantages of the low-*k* films, such as low thermal conductivity and poor mechanical strength.[1,2]

We have proposed novel porous silica film incorporated with ethylene groups which has the potential ability to solve these problems.[3,4] This film showed k=1.9. Although the porous silica film has its *k*-value lower than 2, its Young's modulus and hardness calculated by the loading and unloading characteristics were 4.5GPa and 1.5GPa, respectively.[5] These values were higher than those of conventional porous film having k<2. In this paper we have evaluated porogen desorbing temperature dependence.

2. Preparation of porous silica films incorporated with ethylene groups.

Wet gels were synthesized by the sol-gel reaction with hydrolysis and condensation of BIS (Triethoxysilyl) Ethylene [BTE:$(C_2H_5O)_3SiC_2H_4Si(C_2H_5O)_3$] as a precursor. We chose an organic solvent to form pores after coating, 2-methyl-pentane-2,4-diol [MPD:$CH_3CH(OH)CH_2C(OH)(CH3)_2$]. MPD acts as a high hydrolytic stabilizer and a special kind of drying control chemical additive. The mixture of BTE and MPD whose molar ratio was 1:10 was then processed to gelation by adding water and a catalyst of HCl (0.15 mol/l). This was then stirred at 60 °C for 60 min until the mixture became an appropriate viscosity. The H_2O content in the gel was controlled by distillation after synthesis. The MPD was desorbed from the film by using vacuum annealing at 450°C. We chose vacuum annealing to avoid oxidizing and degrading film quality for desorbing MPD. We have also prepared gel using C_2H_5OH instead of MPD as a reference.

3. Experimental results

Figure 1 shows the density of the low-k film as a function of annealing time. The open diamonds, squares, and triangles represent samples annealed at 350°C, 375°C and 400°C. The open circle represents the result of the sample annealed at 450°C as a reference. The density ρ of the film was calculated from the equation of the total X-ray reflection angle θ_C,

$$\theta_C \approx \left(5.4\times10^{10}\times Z\times\rho\times\lambda^2/A\right)^2\times57.3\,.$$

Where Z is the atomic number and A is the atomic mass.[6] The samples were prepared at R_m=1.The sample annealed at 400°C for 2 hours showed ρ= 1.12g/cm^3. The sample annealed at 375°C for 2 hours showed ρ= 1.22g/cm^3. This value reduced with increasing annealing time, and after 8 hours of annealing the density ρ went down to 1.09g/cm^3, which was almost the same as the ρ after annealing at 450°C for 2 hours. The sample annealed at 350°C for 2 hours showed ρ = 1.39 g/cm^3, and the density ρ reduced with increasing time. The slope of the graph of this sample was the same as those of annealing at higher temperatures, however ρ = 1.25g/cm^3 was obtained even after 8 hours of annealing. We confirmed that the *k*-values of the films having ρ =1.1g/cm^3 were about 1.9.

Figure 2 shows wide mass-range thermal desorbed spectra [TDS] of the film which dried at 150°C. Temperature raising as fast as 60°C/min. Peaks due to MPD was observed at the mass numbers 43 and 59. These peaks were observed in the temperature range between 240 to 400°C. The large peaks in the lower mass-number range (<30) are due to remaining ethyl groups in the BTE.

Figure 3 shows the wide mass-range TDS for the sample after vacuum annealed at 375°C for 8 hours. The peaks around 28 was observed at the temperature range over 500°C. This is due to degradation of porous silica with ethylene groups. The peak due to MPD was not observed in the spectrum. Thus we have concluded that MPD was desorbed from the film after annealing at 375°C, and this result was same as the density change as shown in figure 1.

4. Conclusions

We evaluated MPD desorbing temperature dependence. The porogen (MPD) desorbed from the film in the lower annealing temperature range from 375°C to 400°C. It can be concluded that this temperature range is acceptable for the ULSI process.

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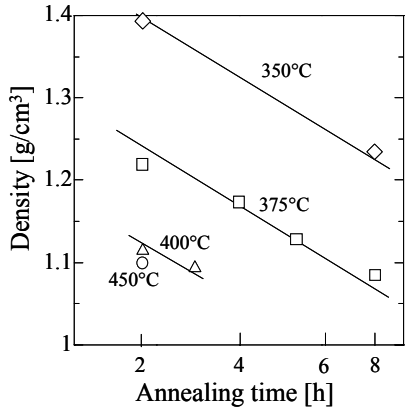

Fig. 1 The density of low-k film as a function of annealing time.

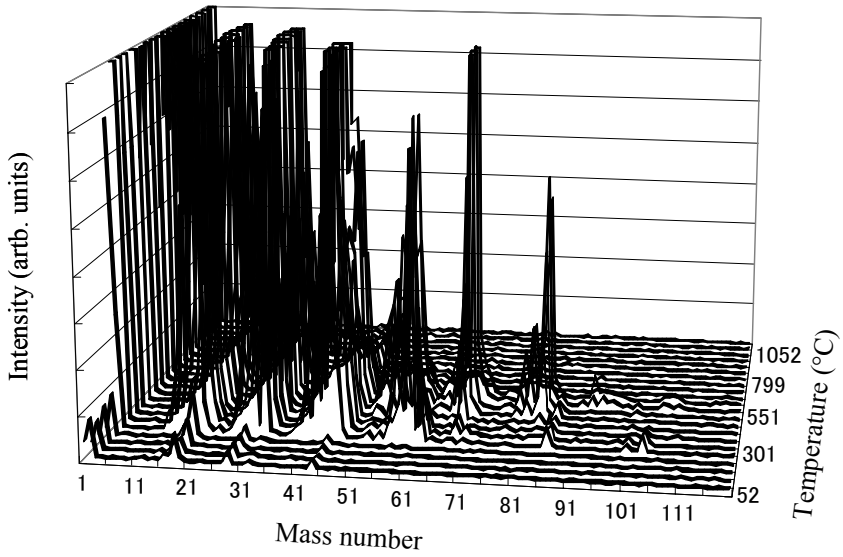

Fig. 2 TDS spectrum of film before vacuum annealing.

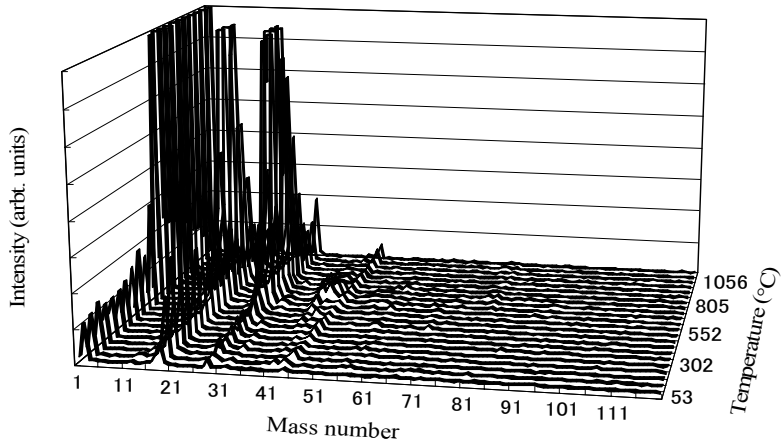

Fig. 3 TDS spectrum of film after vacuum annealing at 375°C for 8 hours.