

# Simple Models on Enhancement of Mechanical Properties of Porous Silica Low-k Films by Tetramethylcyclotetrasiloxane(TMCTS) Vapor Annealing Treatment

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## 1. Introduction

In order to reduce the RC time delay of ULSI circuits, low-resistance interconnect metals and ultra low-dielectric constant (Low-k) interlayer films should be used. One candidate of ultra-Low-k materials is porous silica films, in which main strategy is the reduction of the film density by introducing nanometer sized pores [1,2]. It is, however, suffering from great reduction of mechanical strength, such as elastic modulus and hardness.

Recently, a novel organosiloxane vapor annealing technique with 1,3,5,7-Tetramethylcyclotetrasiloxane (TMCTS) which drastically improves the mechanical properties of porous silica Low-k materials has been developed [3,4]. It was shown that the Young's modulus and hardness was steeply increased by TMCTS vapor annealing above 350°C and exceeded two times of those of non-processed films at 400°C. It was suggested that polymerized TMCTS networks were formed on porous silica wall surfaces and resulted in reinforcement of pore structures.

In this paper, we present simple phenomenological models on the mechanism of the enhancement of mechanical strength of the porous silica Low-k films by TMCTS vapor annealing treatment.

## 2. Enhancement of Mechanical Properties of Low-k Films

Figure 1 shows Young's modulus and hardness of the porous silica Low-k films as functions of TMCTS vapor annealing temperatures [4]. As mentioned above, the process temperature dependences of both modulus and hardness show characteristic behavior.

TMCTS annealing time dependence of Young's modulus is shown in Figure 2. TMCTS process temperature in this case was kept at 400°C. The modulus sharply increased with treatment time up to 10 min and tended to saturate over 10 min.

## 3. Proposed Models

First, we will formulate a simple model to explain TMCTS process temperature dependence of enhancement of Young's modulus.

We assume that effective Young's modulus of TMCTS processed Low-k films  $E_{eff}$  is approximately described by a simple composite law as:

$$E_{eff} = E_0 + (E_1 - E_0) \cdot \theta(T), \quad (1)$$

where,  $E_0$ ,  $E_1$  and  $\theta(T)$  are the Young's modulus of as-deposited Low-k film, the ultimate Young's modulus when TMCTS-derived silica networks fully cover the pore walls, and the coverage factor of the network which is a function of TMCTS process temperature  $T$ , respectively.

Based on the chemical equilibrium theory, we can assume that the functional form of  $\theta(T)$  as:

$$\theta(T) = \frac{A \cdot \exp(-E_a/RT)}{1 + A \cdot \exp(-E_a/RT)}, \quad (2)$$

where  $A$  is a constant and  $E_a$  is the activation energy for chemical reaction associated with building TMCTS-derived silica networks.  $R$  and  $T$  are the gas constant and the absolute temperature, respectively.

If we plot the experimental values of

$$\ln \left[ \frac{\theta(T)}{1 - \theta(T)} \right] = \ln \left( \frac{E_{eff} - E_0}{E_1 - E_{eff}} \right)$$

against  $1/T$ , we can find the 'over all' activation energy  $E_a$  for formation of the additional silica network reinforcing pore walls. The magnitude of the activation energy  $E_a$  is the key parameter to elucidate further the details of the chemical reaction processes which control the formation of the TMCTS networks.

Next, we will consider the annealing time dependence. We assume that the effective Young's modulus  $E_{eff}$  depends on TMCTS process duration is also described by the simple composite law as in the case of Eq. (1), while the coverage factor  $\theta$  is then a function of time in stead of temperature.

We suppose that the rate of reaction of the formation of TMCTS network bonds controlled by the conversion process of Si-H groups of TMCTS to Si-OH groups through hydration by desorption of  $H_2O$ , prior to the

production of Si-O-Si bonds by dehydration between Si-OH groups of adjacent TMCTS, as suggested by Kohmura et al.[4]. The rate equation then can be simply described by:

$$\frac{dn}{dt} = k \cdot (a - n) \cdot (b - n), \quad (3)$$

where  $n$  is the density of the reaction product, namely, the TMCTS network bonds,  $a$  and  $b$  are the densities of Si-H in TMCTS and H<sub>2</sub>O molecules, and  $k$  is the rate constant. Supposing  $\theta(t)$  is proportional to  $n$ , the time evolution of the coverage factor of the TMCTS networks over pore walls is described by:

$$\theta(t) \propto \frac{ab(e^{kbt} - e^{kat})}{b \cdot e^{kbt} - a \cdot e^{kat}}. \quad (4)$$

#### 4. Results of Model Fitting and Discussion

Figure 3 shows the Arrhenius plot of  $\theta(T)$ , assuming that  $E_0$  is 4.26GPa for non-processed film and  $E_1$  is 11GPa. We obtained the activation energy  $E_a$  of 60.3kJ/mol as the slope of the plot. Fitted result of TMCTS process temperature dependence of Young's modulus is plotted in Fig. 1. The simple theoretical model agrees well with the experimental values as expected by Eqs. (1) and (2).

TMCTS annealing time dependence of Young's modulus is also well-described by the simple reaction model of Eq. (4) as shown in Fig. 2.

Both TMCTS annealing temperature and time dependence of enhancement of Young's modulus were well explained by the proposed models including a few model parameters. This suggests that only limited rate-determining steps control the formation of TMCTS networks on pore wall surfaces, even though the reaction processes are quite complicated.

#### 5. Conclusions

We have presented the simple theoretical models to explain both the process temperature dependence and the process duration dependence of the enhancement of Young's modulus of porous silica Low-k films by TMCTS vapor annealing treatment.

The model fittings agreed well with the experimental results obtained by Kohmura et al. The apparent activation energy for chemical reaction of formation of TMCTS-derived silica networks was obtained as 60.3kJ/mol.

To verify that this activation energy is quantitatively appropriate or not, further investigations on elementary chemical reaction processes of formation of TMCTS network bonds in porous silica Low-k materials are needed.

#### Acknowledgement

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#### References

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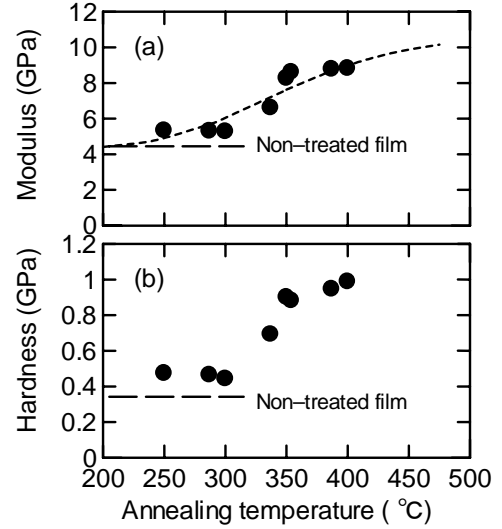


Fig. 1 Effects of TMCTS vapor annealing temperature on (a) Young's modulus and (b) hardness of porous silica films. Dotted line shows the model fitting of Eqs. (1) and (2).

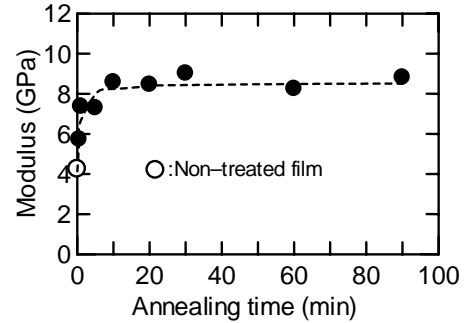


Fig. 2 Effects of TMCTS vapor annealing time on Young's modulus of porous silica films. Dotted line indicates the fitted result of time evolution model of Eq. (4).

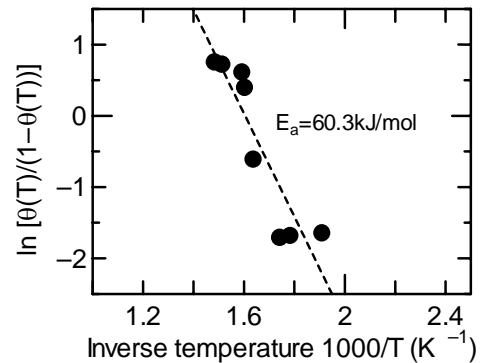


Fig. 3 Arrhenius plot of the coverage factor  $\theta(T)$ . Dotted line shows the linear regression to inverse temperature giving the activation energy  $E_a$  of 60.3kJ/mol.