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Theory of Dielectric Constant in Porous Materials

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The porosity dependence of dielectric constant in porous materials is studied theoretically in relation with low dielectric constant materials in the field of advanced semiconductor technology. We have developed a theory that takes into account the charging effect of pore surfaces self-consistently. The present theory predicts that the dielectric constant decreases more rapidly than expected by previous models when the porosity increases. This reflects the charging effect of pore surfaces and is remarkable for porous materials of higher dielectric constant and with finer pores. The present theory suggests that porous materials with regularly arranged and nanometer-sized pores are promising low dielectrics for future semiconductor integrated circuits devices. Some suggestions as to experimental studies will be given on the basis of the present theory.

Key words: theory, dielectric constant, nanoporous materials, porosity

1. INTRODUCTION

Porous materials have been used for various purposes such as adsorbents, gas sensors, catalyst supports and heat insulating materials. In recent years, porous materials as their electrical property are being studied for the purpose of developing low dielectric constant (low-*k*) materials for integrated circuit applications[1]. The development of porous dielectrics as low-*k* materials is one of important subjects in the field of advanced semiconductor technology.

In microelectronic device technology, the continuing improvement of microprocessor performance involves decreasing device size. As the device dimension shrinks, propagation delay, cross talk noise and power dissipation increase. To address resistance and capacitance delay, new materials with low-*k* dielectrics are being developed to replace conventional silicon dioxide as interlayer dielectrics. One of the most promising candidates is nanoporous silica.

In order to develop low-*k* nanoporous dielectrics, it is important to understand well dielectric properties of porous materials. In this paper the relation between the dielectric constant and the porosity of nanoporous materials is theoretically investigated. We develop a theory that takes into account the charging effect of pore surfaces self-consistently. The theory is compared with conventional models and experimental data, and is discussed in the context of the design of low-*k* nanoporous materials.

2. PREVIOUS STUDIES

Measurements of dielectric constant in porous materials have been done by many authors. Experimental data on the relative dielectric constant k versus the porosity ϕ in some porous ceramics are shown in Fig. 1, where the relative dielectric constant is the value to that of vacuum and the porosity is the volume fraction of pores. From the theoretical side, a variety of models have been proposed for the porosity dependence of dielectric constant. A simple model is the mixing rule for laminar composites connected in series or in parallel. This model gives

$$k = k_0(1-\phi)+\phi \qquad \text{(in parallel)} \qquad (1)$$

$$k = k_0(1-\phi+k_0\phi)^{-1} \qquad \text{(in series)} \qquad (2)$$

where k_0 is the value at $\phi = 0$. Figure 2 shows the series and parallel model of porosity dependence of k/k_0 for $k_0 = 2$, 4 and 10. Experimental data as shown in Fig. 1 are distributed between two curves given by equations (1) and (2).

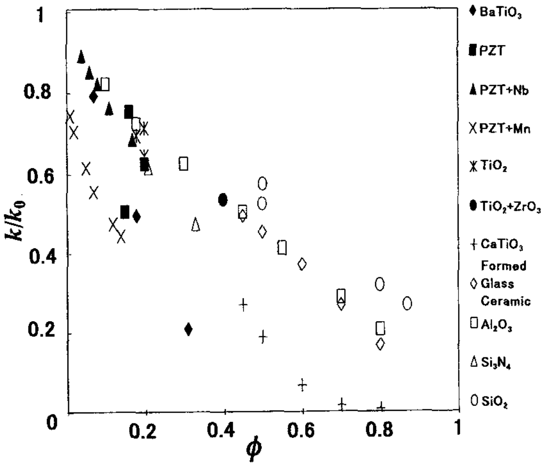

Fig. 1 Experimental data[6-14] of the porosity dependence of the relative dielectric constant in porous ceramics.

Other expressions of dielectric constant of porous materials as heterogeneous systems have been derived theoretically by several authors such as Bruggeman[2], Bottcher[3] and Looyenga[4]. Also, a study based on computer simulation has been reported by Wakino *et al.*[5] Comparison between theory and experiment to judge the validity of models is somewhat difficult because experimental data is scattered from sample to sample.

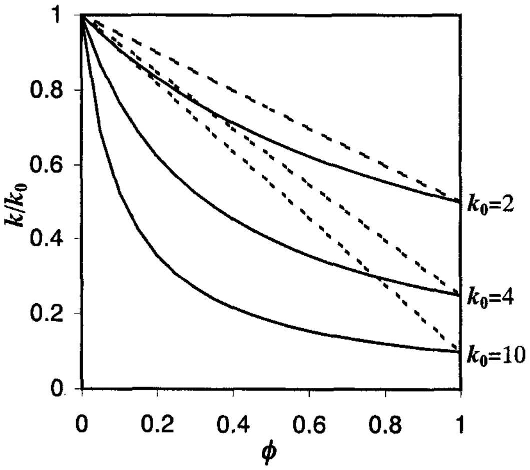

Fig. 2 The porosity dependence of k/k_0 for $k_0 = 2$, 4 and 10 in the mixing rule for laminar composites connected in series (solid curves) and in parallel (dashed curves).

3. THEORY

Because the thickness of interlayer dielectrics in microelectronic devices is as thin as micrometer, porous materials with nanometer-sized pores is required for interlayer dielectrics. In those nanoporous materials the effect of charging of pore surfaces on dielectric constant should be addressed. We here develop a model that takes into account the charging effect self-consistently.

Consider a nanoporous material with the averaged polarization P and the averaged electric field E, as shown in Fig. 3.

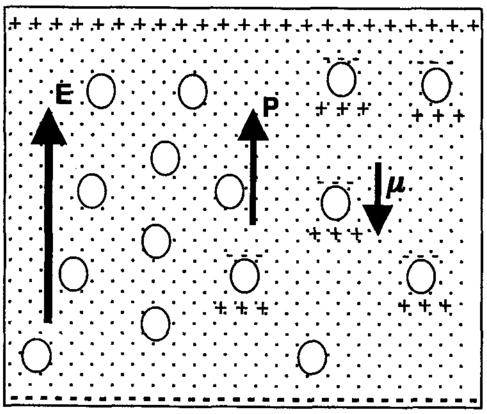

Fig. 3 Schematic view of polarized nanoporous materials with the polarization P and the electric field E.

Then the polarized charges appear on the surface of each pore. These polarized charges can be regarded as electric dipole moments distributed in the material. Therefore the polarization P of the material consists of the contributions of both the solid phase and the dipole moments of pores as

$$P = P_0 + P' \tag{3}$$

where P_0 and P' are the contribution of the polarizations from solid phase and pores, respectively.

The polarization of the solid phase can be expressed on the assumption that the material without pores is composed of N polarized molecules. Since the solid phase of the material with porosity ϕ includes $N(1-\phi)$ polarized molecules, the polarization of the solid phase is given by

$$P_0 = N(1-\phi)\alpha\left(E + \frac{P}{3\varepsilon_0}\right) \tag{4}$$

where ε_0 is the dielectric constant of vacuum and α is the polarizability of a molecule. We have used the Lorentz's local field, $P/3\varepsilon_0$, for the local electric field at the site of a molecule.

The contribution of the dipole moments of polarized charges on pore surfaces can be derived by assuming spherical pores distributed uniformly in a material. When there are N' pores per unit volume, the polarization of pores is given by

$$P' = N'\mu \tag{5}$$

where μ is the electric dipole moment of a pore and is related with the averaged polarization of the material P by

$$\mu = -\left(\frac{4}{3}\pi a^3\right)P \tag{6}$$

where a is the radius of a spherical pore. It should be noted that the direction of μ is opposite to that of P. From equations (5) and (6), we get

$$P' = -\phi P \tag{7}$$

where we have noticed that the volume of pores per unit volume, $N'(4\pi a^3/3)$, is equal to the porosity ϕ.

Substituting equations (4) and (7) into (3), we have

$$P = N(1-\phi)\alpha\left(E + \frac{P}{3\varepsilon_0}\right) - \phi P \tag{8}$$

Since the right side of equation (8) includes P, we solve P self-consistently. The result is given by

$$P = \frac{N(1-\phi)\alpha}{(1+\phi)\,\varepsilon_0 - (1/3)N(1-\phi)\alpha}\,\varepsilon_0 E \tag{9}$$

Since the relative dielectric constant k is defined by

$$k = 1 + \frac{P}{\varepsilon_0 E} \tag{10}$$

we obtain from equations (9) and (10),

$$k = 1 + \frac{N(1-\phi)\alpha}{(1+\phi)\,\varepsilon_0 - (1/3)N(1-\phi)\alpha} \qquad (11)$$

When $\phi = 0$, equation (11) gives the relative dielectric constant without pores k_0 as

$$k_0 = \frac{\varepsilon_0 + (2/3)N\alpha}{\varepsilon_0 - (1/3)N\alpha} \qquad (12)$$

From equations (11) and (12), the relative dielectric constant of porous materials is represented in terms of k_0 and ϕ by

$$k = \frac{(k_0+2)(1+\phi) + 2(k_0-1)(1-\phi)}{(k_0+2)(1+\phi) - (k_0-1)(1-\phi)} \qquad (13)$$

$$= \frac{3k_0 - (k_0-4)\phi}{3 + (2k_0+1)\phi} \qquad (14)$$

Figure 4 shows the porosity dependence of k/k_0 in equation (14) for k_0 = 2, 4 and 10. These curves as a result are close to those in the mixing rule connected in the series model as shown in Fig. 2. This reflects the charging effect of pore surfaces, which reduces the averaged polarization of a material.

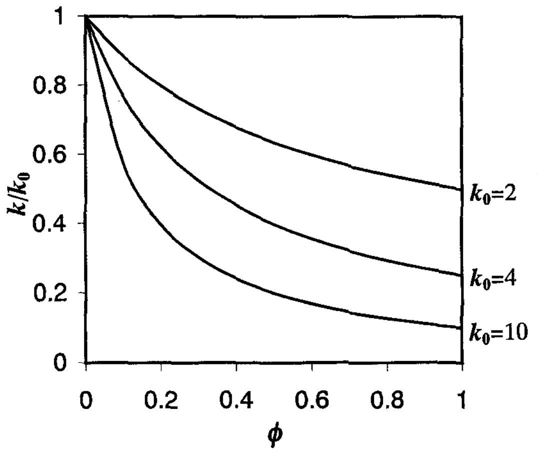

Fig. 4 The porosity dependence of k/k_0 for k_0 = 2, 4, and 10 in the model that takes into account the charging effect of pore surfaces.

The contribution of the charging effect of pore surfaces to the averaged polarization is manifested by the dependences of P_0, P' and P on porosity ϕ. From equations (3), (4), (7) and (9), we get

$$P_0 = \frac{3(k_0-1)(1-\phi)(1+\phi)}{(k_0+2)(1+\phi) - (k_0-1)(1-\phi)}\,\varepsilon_0 E \qquad (15)$$

$$P' = -\frac{3(k_0-1)\phi(1-\phi)}{(k_0+2)(1+\phi) - (k_0-1)(1-\phi)}\,\varepsilon_0 E \qquad (16)$$

$$P = \frac{3(k_0-1)(1-\phi)}{(k_0+2)(1+\phi) - (k_0-1)(1-\phi)}\,\varepsilon_0 E \qquad (17)$$

Figure 5 shows the porosity dependence of P_0, P' and P in the present model. The effect of polarized charges on pore surfaces, P' is most efficient at ϕ = 0.35. As the porosity increases from zero, the inverse polarization of pores increases to reduce the whole polarization. However the inverse polarization becomes small at large porosity because the whole polarization becomes small.

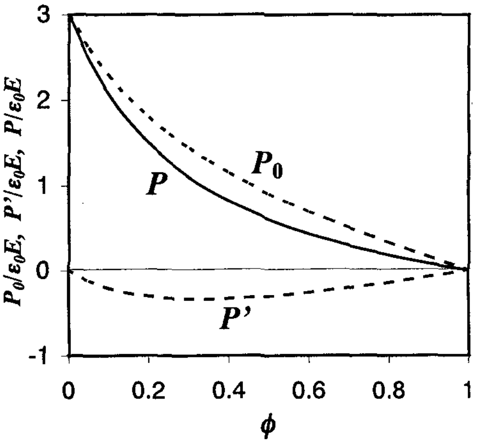

Fig. 5 The porosity dependence of the polarizations P (solid curve), P_0 (upper dashed curve) and P' (lower dashed curve) for k_0 = 4 in the model that takes into account the charging effect of pore surfaces.

4. DISCUSSION

The present model predicts that the relative dielectric constant k decreases more rapidly than expected by previous models[2-5] when the porosity ϕ increases. The predicted dependence of k on ϕ is rather close to the mixing rule of the series model, which corresponds to the lower bound for laminar composite model. This reflects the charging effects of pore surfaces, which reduces the whole polarization of porous materials. This effect is also remarkable for porous materials of higher dielectric constant. If we neglect the charging effect, that is, if P' = 0 in equation (3), then we can get

$$k = \frac{(k_0+2) + 2(k_0-1)(1-\phi)}{(k_0+2) - (k_0-1)(1-\phi)} \qquad (18)$$

$$= \frac{3k_0 - 2(k_0-1)\phi}{3 + (k_0-1)\phi} \qquad (19)$$

This result is identical with the expression given by Bruggeman[2]. Equation (18) should be compared with equation (13). We see that the charging effect of pore surfaces is reflected by the factor $(1+\phi)$. The comparison between equations (13) and (18) is shown in Fig. 6.

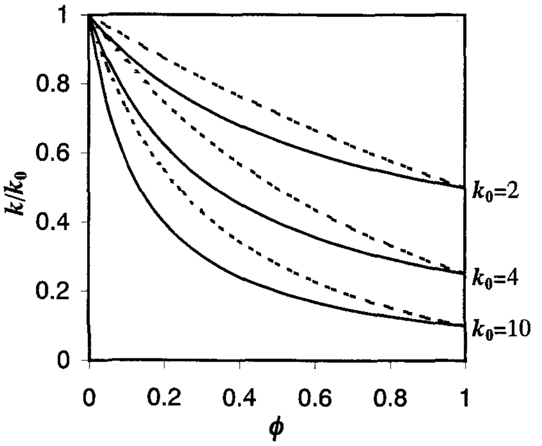

Fig. 6 Comparison between the models with (solid curve) and without (dashed curve) the charging effect of pore surfaces for $k_0 = 2$, 4, and 10.

The comparison between the present model and available experimental data is shown in Fig. 7. We have cited experimental data on SiO_2 with $k_0 \sim 4$ and Al_2O_3 and Si_3N_4 with $k_0 \sim 10$, which are compared with the curves for $k_0 = 4$ and $k_0 = 10$ from equation (14) of the present model. The experimental data show larger dielectric constants than those predicted by the present model. This may be attributed to the fact that the size of pores in the measured samples is in the order of micrometer, while we assumed nanometer-sized pores, as discussed below.

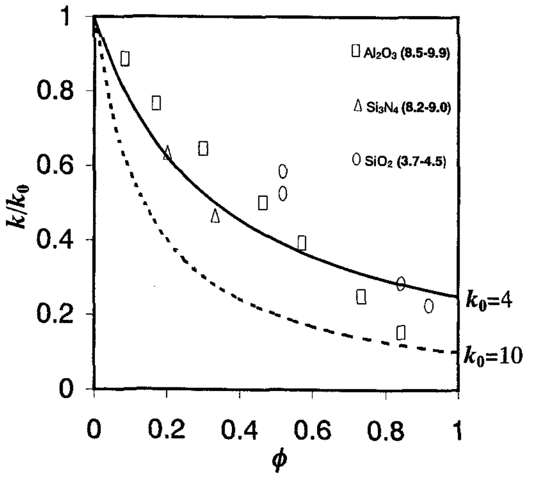

Fig. 7 Comparison between the present model and experimental data.

Although there are many experimental data on the porosity dependence of dielectric constant in porous materials, those data are not sufficient because they are rather scattered from sample to sample and because there are very little data measured over a wide range of porosity. Furthermore the reported data are concerned with samples with micrometer-sized pores. The charging effect of pore surfaces is considered to be more efficient for finer pores. Therefore we expect that measurements are given for nanoporous materials over a wide range of porosity.

In the present model, we have assumed a material in which nanometer-sized pores are distributed uniformly in the material and the shape of a pore is spherical. Also we have used the Lorentz's local field for the local electric field at the site of a molecule that is satisfied in uniformly and regularly arranged pores. These assumptions are not necessarily satisfied in real porous materials developed until now. Thus we expect that porous materials with regularly arranged and nanometer-sized pores will be developed for promising low-*k* dielectrics.

5. CONCLUSION

Nanoporous materials are one of promising low-*k* dielectrics in advanced microelectronic devices. We have presented a theory that takes into account the charging effect of pore surfaces in nanoporous materials. The theory suggests that the dielectric constant of nanoporous materials decreases rapidly with increasing porosity due to the charging effect of pore surfaces. The development of nanoporous materials with uniformly and regularly arranged pores is expected for the realization of low-*k* dielectrics.

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