

Effect of O₂ plasma treatment on the properties of SiO₂ aerogel film

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Abstract

In the down-scaling trend of ultra large scaled integration, SiO₂ aerogel film can be a promising material for intermetal dielectric with inherent low dielectric constant. A TEOS-derived SiO₂ aerogel film by spin-coating and supercritical drying has high porosity and large internal surface area which contains the chemical species on the internal surface, such as organic groups, hydroxyl groups, and adsorbed water. An oxygen plasma treatment of SiO₂ aerogel film was introduced to control the internal surface chemical species for applying to intermetal dielectrics. The chemical bonding state of the internal surface, microstructure, and electrical properties of the oxygen plasma treated SiO₂ aerogel film were analyzed. Through the oxygen plasma treatment, the surface chemical groups were effectively eliminated. Also, with the parameter changes of oxygen plasma treatment such as ICP power and bias voltage, micro-structural evolution occurred. Decreases in thickness and particle growth were observed. And the improvement of leakage current behavior was also observed after oxygen plasma treatment. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: SiO₂ aerogel; IMD; Low dielectric; Oxygen plasma; Plasma treatment

1. Introduction

The performance and reliability of ultra large scaled integration (ULSI) devices strongly depends on the interconnection system. Interconnection delay, generally termed resistance–capacitance (*R–C*) time delay, which is mainly dominated by parasitic capacitance between metal interconnections, has received a great deal of attention over the basic gate delay in the deep submicron devices [1–3]. Therefore, low *k* (i.e. low dielectric constant) materials which substitute for conventional intermetal dielectric (IMD) have become imperative for the reduction of parasitic capacitance between multi-metal layers. Sol-gel derived SiO₂ aerogel film is one of the prospective candidates for IMD material since a very low dielectric constant can be achieved from its inherent high porosity. It is also highly compatible with existing microelectronic precursor materials. It has been shown that bulk type of SiO₂ aerogel can easily show extremely high porosity up to 95%, with corresponding dielectric constant of approximately 1.0 [4,5]. Due to its unique characteristic, SiO₂ aerogel film has been applied as IMD [6]. In our earlier work, a SiO₂ aerogel film with 67% porosity was prepared and it had static dielectric constant value of around 2.1 at 1 MHz in an MIS (metal/insulator/semiconductor) structure [6].

From studies of the characteristics of sol-gel derived processes, the skeletal network of SiO₂ aerogel films contains a number of Si–OR (R, alkoxy group), Si–OH bonds and adsorbed water as internal surface species. The degradation of the electrical properties such as dielectric constant and leakage current density were observed due to the above highly polarizable species.

In this work, a possible application of O₂ plasma treatment using inductively coupled plasma (ICP) to SiO₂ aerogel films at room temperature was introduced for the control of internal surface chemical species in the film. Among several high-density plasma sources, ICP was used because a high electron density of 10¹² cm⁻³ could be easily obtained below 10⁻² Torr without an additional magnetic field [7–9]. The physical, chemical, and electrical effects of O₂ plasma treatment on SiO₂ aerogel film were investigated.

2. Experimental procedures

SiO₂ sol used in this experiment was prepared by a two-step process involving acid and base catalysts with tetraethoxylane (TEOS) as a precursor. We used iso-propyl alcohol (IPA) as a solvent because it has relatively low critical temperature and pressure in the supercritical drying process [10]. The composition of sol was TEOS/H₂O/NH₄OH/HCl/IPA=1:4:8.2 × 10⁻³:1.8 × 10⁻⁴:3 molar ratio. The gelation was accomplished in 10 h at room temperature. The

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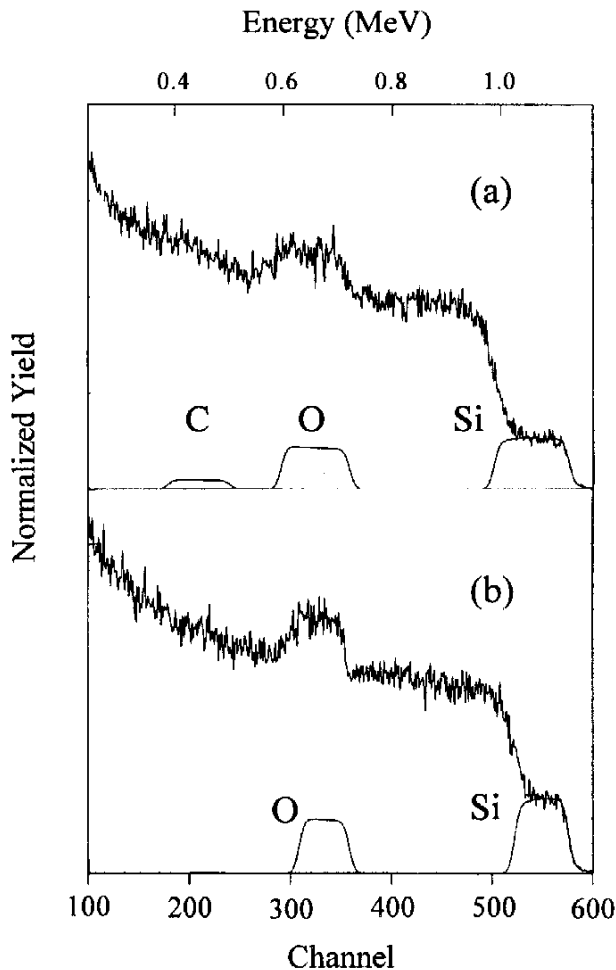


Fig. 1. Compositions of SiO₂ aerogel films obtained using RBS; (a) as-prepared and (b) oxygen plasma treated.

sol was spin-deposited on p-type Si(100) wafer using a commercial photo-resist spinner in the optimized viscosity range with the spin rate of 3000 rev./min for 20 s under the solvent atmosphere to minimize the solvent evaporation from SiO₂ wet gel. Then each spun-on film was immersed in IPA for 24 h and subsequently placed in an autoclave apparatus. The solvent could be extracted from the internal pores between skeletal solid fraction without any shrinkage through the supercritical drying treatment. After the supercritical drying process, the samples were subjected to an O₂ plasma treatment at room temperature. For the O₂ plasma treatment, an ICP equipment of a commercial 13.56 MHz parallel-plate plasma reactor was used. The inductive power, the bias voltage, and the exposure time to O₂ plasma were varied from 400 to 600 W, from 0 to 10 V, and from 30 to 900 s, respectively. The background pressure was 20 mTorr and the operation pressure was maintained at 40 mTorr. The substrate temperature was 3°C.

The surface morphology and thickness of films were investigated by scanning electron microscope (SEM, Hitachi S-4200). The film density/porosity and chemical composition were complementarily determined by Rutherford

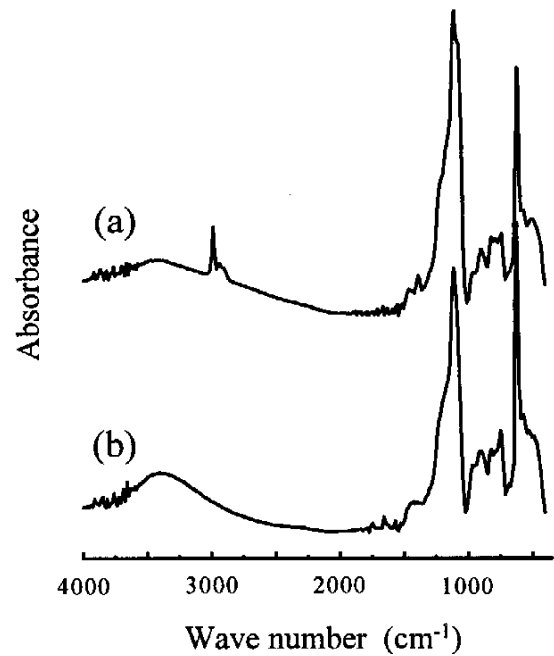


Fig. 2. Internal surface coverages of SiO₂ aerogel films obtained using FTIR; (a) as-prepared and (b) oxygen plasma treated.

backscattering spectrometry (RBS, NEC 6-SDH) with collimated 2 MeV He²⁺ ions and cross-sectional SEM. Elastic recoil detection (ERD) method was also employed to detect hydrogen content before and after the treatment. To investigate the changes of chemical species and surface chemical bonding states after the O₂ plasma treatment, Fourier transform infrared spectroscopy (FTIR, Bohmem DA 3.16 Spectrophotometer) and X-ray photoelectron spectroscopy (XPS) were used. XPS analysis was performed with a V.G. Scientific ESCALAB 220i-XL spectrometer using Mg K α (1253.6 eV) radiation operating at 250 W. Narrow scan spectra of all regions of interest were recorded in order to quantify the surface composition and identify the elemental bonding states with pass energy of 20 eV and take-off angle of 90°. Leakage current behavior was evaluated using HP 4155A semiconductor parameter analyzer on a MIS structure, which was fabricated by depositing an Al electrode at room temperature onto SiO₂ aerogel film using a thermal evaporator. The back side of the Si wafer also was metallized after etching off the native oxide with a diluted HF solution in order to form a better back contact.

3. Results and discussion

The typical RBS spectra obtained from both as-prepared and oxygen plasma treated SiO₂ aerogel films are shown in Fig. 1. The composition of films, e.g. ratios of O/Si and C/Si, could be deduced by comparing the yield heights of the elements in the spectra [11,12]. The atomic ratio of Si/O/C was measured to be 1:2.5:1.0 for the as-prepared SiO₂ aerogel film and 1:2.1:0.03 for the oxygen plasma treated

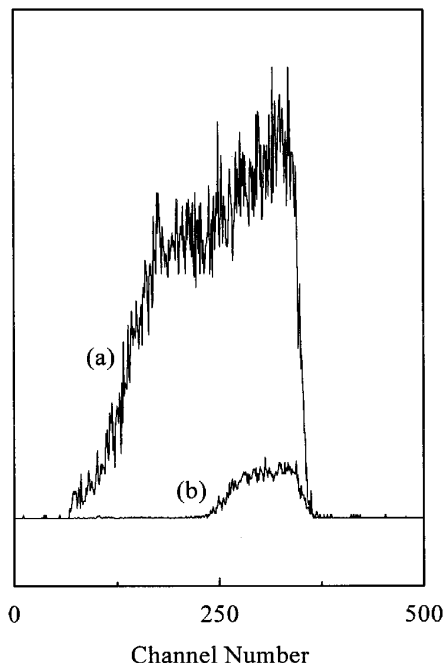


Fig. 3. Residual hydrogen contents of SiO₂ aerogel films obtained using ERD; (a) as-prepared and (b) oxygen plasma treated.

SiO₂ aerogel film. The carbon content in the films decreased drastically after the oxygen plasma treatment. The carbon species are from the partially hydrolyzed TEOS and residual IPA used as a precursor and solvent, respectively. Also, the O/Si ratio was reduced, closer to 2, for the oxygen plasma treated film and it was caused by the reduction in the internal

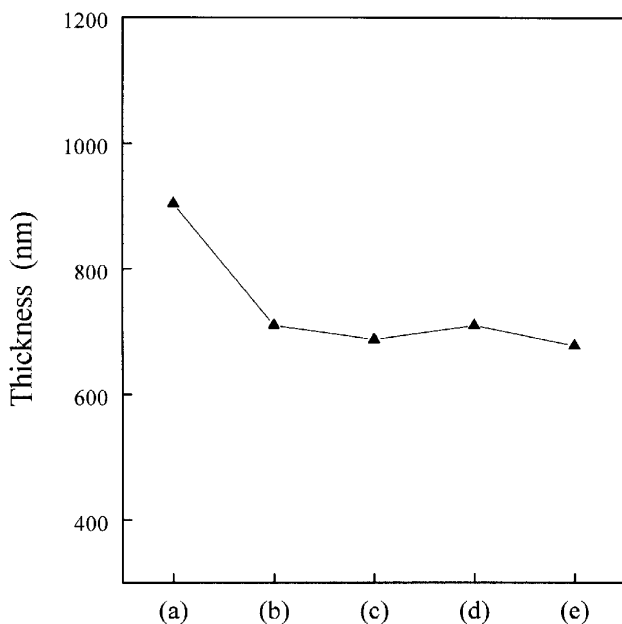


Fig. 4. Variation in the thickness of SiO₂ aerogel films; (a) as-prepared and oxygen plasma treated for (b) 30 s, (c) 1 min, (d) 5 min and (e) 15 min.

surface organic of SiO₂ aerogel film. The O/Si ratio can be a useful parameter to judge the quantity of Si—OR and Si—OH bonds on the internal pore surface (the stoichiometry of O/Si is 2 for ideal SiO₂).

FTIR absorbance spectra were used to identify the internal surface coverages before and after the oxygen plasma treatment. As shown in Fig. 2, the most intense absorption peak which constitutes the skeletal SiO₂ network is located at 1060–1080 cm⁻¹ due to the asymmetric stretching vibration of Si—O bond. Besides skeletal Si—O peak, various C—H stretching peaks around 2936 and 2978 cm⁻¹ are observed with their deformation peaks around 1380 and 1467 cm⁻¹ in as-prepared SiO₂ aerogel film [13]. From the above results, it was revealed that many ethoxy groups (—OC₂H₅) due to the incomplete hydrolysis of TEOS were remained on the internal surface of as-prepared film. All of the oxygen plasma treated SiO₂ films showed exactly the same IR spectra, regardless of variation in the oxygen plasma treatment conditions. After the oxygen plasma treatment, no C—H stretching peaks are observed as shown in Fig. 2b. A destruction of C—H deformation peaks is also observed. It means that the surface organic groups were effectively eliminated by the oxygen plasma treatment. This result is in agreement with that of RBS analysis. But the existence of Si—OH stretching vibrational peak at 3400–3750 cm⁻¹ was not clear in the oxygen plasma treated film. The elimination of residual hydroxyl group is very important for the application of SiO₂ aerogel film to IMD because the hydroxyl group has a great tendency of moisture absorption which results in the degradation of the film properties. The residual hydrogen content in the film could be revealed by ERD measurement and the results were given in Fig. 3. The content of residual hydrogen was found to be negligible after the oxygen plasma treatment. And then it can be said that the residual hydroxyl group was effectively eliminated through the oxygen plasma treatment.

In Fig. 4, the change of thickness of oxygen plasma treated films with varying the exposure time to oxygen plasma at 400 W of ICP power, with no bias voltage is shown. The thickness of SiO₂ aerogel film was found to be reduced after the oxygen plasma treatment from 900 to 700 ± 10 nm, but it was maintained even with varying the exposure time from 30 s to 15 min.

The surface morphology and thickness of SiO₂ aerogel films obtained after varying the oxygen plasma treatment condition are shown in Fig. 5 and Fig. 6. Fig. 5 corresponds to planar and cross-sectional SEM images of SiO₂ aerogel films before and after the oxygen plasma treatment at 0 V of bias voltage with 400 or 600 W of ICP power for 5 min. The increase in ICP power brought about the growth of particle size only in the uppermost surface layer. With increasing ICP power, the generated self-bias at the electrode increases. The charged particle is accelerated and moves to the film surface by the potential gradient. The collapse of film surface structure can be obtained if the charged

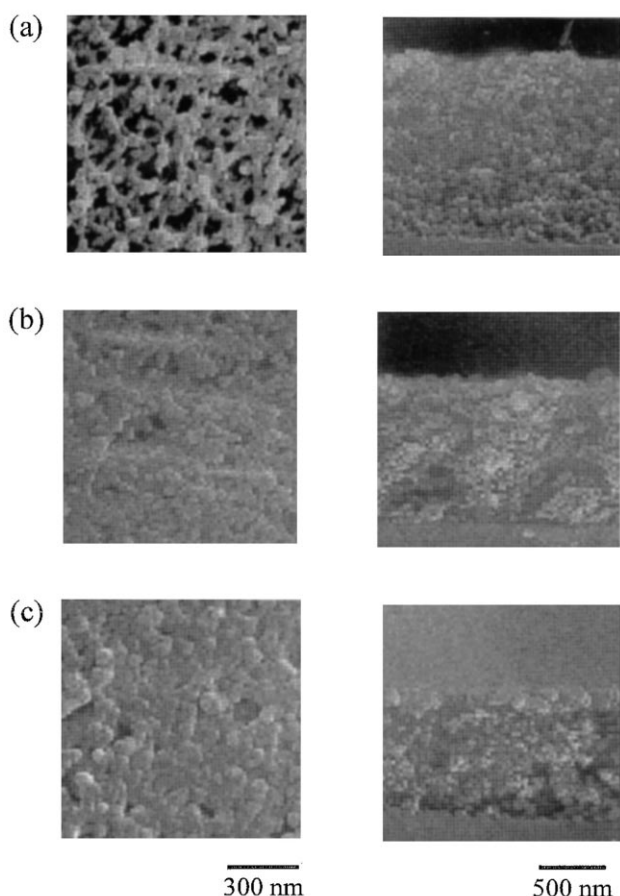


Fig. 5. Planar and cross-sectional SEM images of SiO_2 aerogel films; (a) as-prepared and oxygen plasma treated with ICP power of (b) 400 W and (c) 600 W.

particles have enough energy. When the charged particles with higher energy collapse on the film, their kinetic energy changes to thermal energy and thermal energy can be supplied to the SiO_2 aerogel film. It induces the agglomeration of surface particles and results in the increase of the particle size in the uppermost surface layer. In practical application, this phenomenon could be effectively applicable to prevent the electrode material from permeating to the internal pores of the SiO_2 aerogel film. Even though the thickness of the film reduced from 1400 to 1000 nm after the above oxygen plasma treatment, the porosity of the film decreased by only 5%. This is due to the elimination of the internal surface chemical groups which has double-sided effects. The elimination, itself increases the film porosity. But condensation reaction also occurs during the elimination and results in the decrease of the film porosity [6]. In Fig. 6, SEM images show the effect of bias voltage during the oxygen plasma treatment. As the bias voltage increased from 0 to 10 V with 400 W of ICP power, the particle size of the film surface increased. With 10 V of the bias voltage, the porosity of the film decreased by 5% compared with that of as-prepared film. The effect of applying bias voltage during the oxygen plasma treatment on the

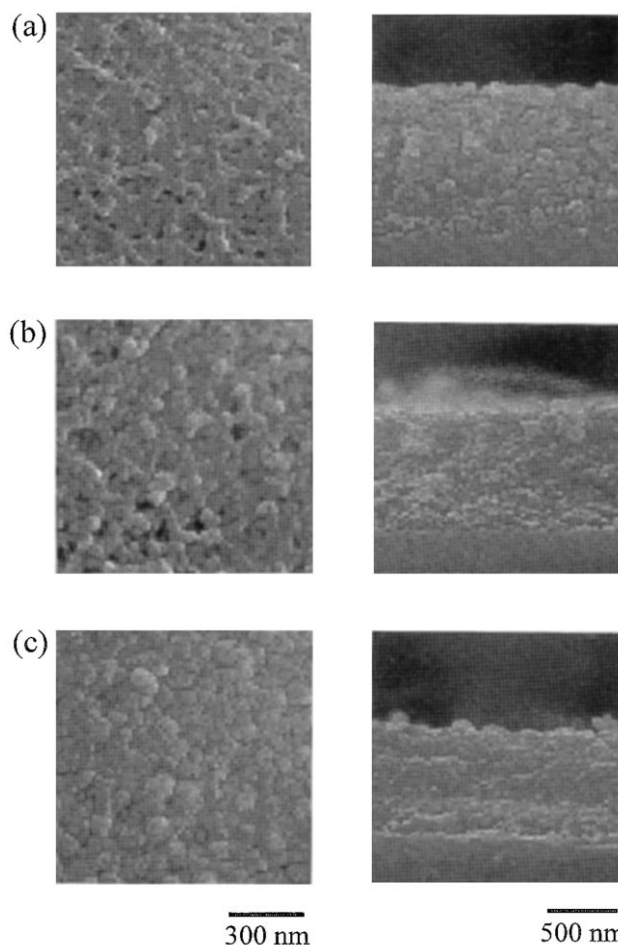


Fig. 6. Planar and cross-sectional SEM images of SiO_2 aerogel films; (a) as-prepared and oxygen plasma treated with bias voltage of (b) 0 V and (c) 10 V.

porosity and microstructure of the film was found to be same as the increase of ICP power.

Fig. 7 shows full width at half maximum (FWHM) values of Si 2p and O 1s peaks of the as-prepared and oxygen plasma treated SiO_2 aerogel films obtained using XPS. A slight decrease of FWHM values of Si 2p and O 1s peaks was observed after the oxygen plasma treatment with 400 W of ICP power. And this decrease resulted from the elimination of internal surface chemical bonds. As the ICP power increased from 400 to 600 W, abrupt decrease of FWHM values was observed. This was due to the increase in the particle size which makes the formation of a regular $[\text{SiO}_4]$ tetrahedron more probable.

The leakage current characteristic of the SiO_2 aerogel film at up to 1 MV/cm of applied electric field is shown in Fig. 8. Both the as-prepared and oxygen plasma treated SiO_2 aerogel films were dehydrated in Ar atmosphere at 150°C before the measurements to minimize the effect of physisorbed moisture in the film. The overall characteristics of leakage current density (J) could be depicted in a similar fashion as that as applied electric (E) increased, the leakage current

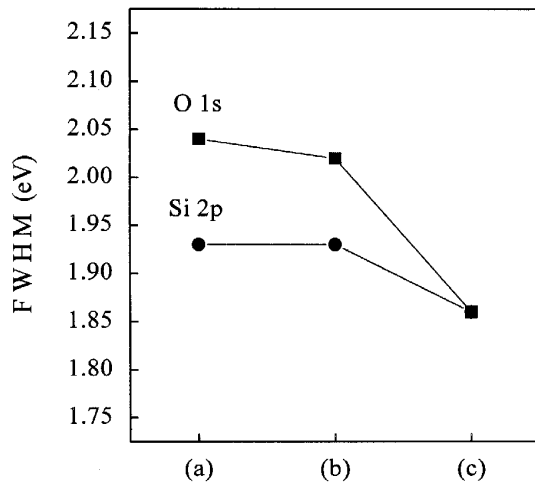


Fig. 7. FWHM values of SiO₂ aerogel films obtained using XPS; (a) as-prepared and oxygen plasma treated with ICP power of (b) 400 W and (c) 600 W.

increased parabolically up to a saturation point. I - V characteristics were evaluated in terms of the amount of residual surface coverages. Overall, better leakage current density was achieved after the oxygen plasma treatment, believed from the removal of surface organic species.

4. Conclusions

The effect of the oxygen plasma treatment on SiO₂ aerogel film was investigated for applying to intermetal dielectrics. The Si/O/C ratio of SiO₂ aerogel film was obtained as 1:2.5:1.0 and 1:2.1:0.03 with the as-prepared and oxygen plasma treated films, respectively. With the treatment, the internal surface chemical groups such as Si-OR and Si-OH were almost removed. Also, the effect of the variation in the oxygen plasma parameters on the microstructure and porosity of SiO₂ aerogel film was investigated. With the increase in ICP power and the introduction of bias voltage, the agglomeration of surface particles and the increase in the particle size were observed. This was accompanied by a decrease in the thickness of SiO₂ aerogel film. However, the porosity of SiO₂ aerogel films decreased slightly, (a few percent) after the oxygen plasma treatments. An improvement of leakage current density was observed. Finally, oxygen plasma treatment was revealed to be an effective method for removing undesirable internal surface chemicals and filling up the porous surface of SiO₂ aerogel films, and this could advance an application of the films to conventional device fabrication processes.

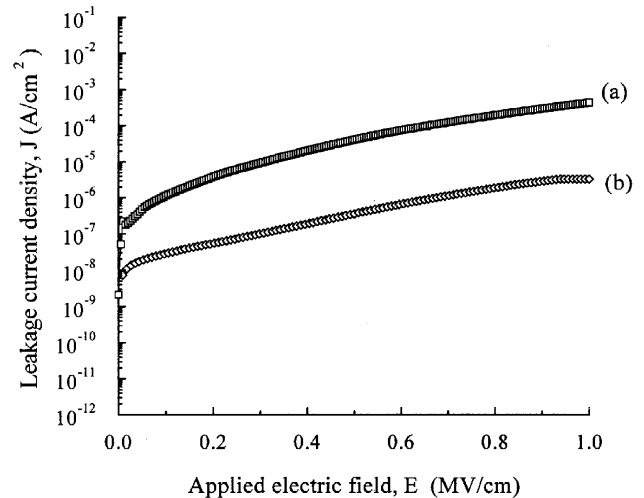


Fig. 8. Leakage current behaviors of SiO₂ aerogel films; (a) as-prepared and (b) oxygen plasma treated.

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