Extended Abstracts of the 2006 International Conference on Solid State Devices and Materials, Yokohama, 2006, pp. 474-475

P-2-7

# Characterization of pore sealing effect on trench sidewalls in porous low-k films by vapor adsorption *in-situ* spectroscopic ellipsometry

N. Hata[1], K. Koga[2], K. Sumiya[2], S. Takada[1], M. Tada[2], Y. Kawamoto[2], and T. Kanayama[1]

[1] MIRAI- Advanced Semiconductor Research Center (ASRC), National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan
[2] Consortium for Advanced Semiconductor Materials and Related Technologies (CASMAT), 1-280 Higashi-Koigakubo, Kokubunji, Tokyo 185-0014, Japan

**Abstract**
Non-destructive characterization of pore sealing effect on trench sidewall of porous low-dielectric-constant (low-k) films by adsorption *in-situ* spectroscopic ellipsometry of 300 mm patterned wafers is reported. It was found that an argon (Ar) plasma pore-sealing process is effective for a porous methysilsesquioxane (MSQ) with a small pore size, but not for a larger.

**Introduction**
While porous films are very attractive for their low dielectric constant as interlayer dielectrics in ultralarge scale integrated (ULSI) circuits, special cares such as non-destructive in-line monitoring of the pore structure as well as the pore sealing need to be taken for back-end-of-line process integration with those films. In this work, we employed a non-destructive characterization technique of vapor adsorption *in-situ* spectroscopic ellipsometry to characterize the pore sealing effect.

**Experimental**
Two kinds of porous MSQ-type low-k films (type A and B, properties shown in Table I) were prepared by spin-coating on silicon wafers of 300 mm in diameter, on which silicon dioxide capping layers were plasma deposited from a silane-oxidant mixture. Pore size distributions (*psd*s) of blanket films of the type A and B determined by adsorption *in-situ* spectroscopic ellipsometry analysis are shown in Fig. 1. Trench patterns were formed by dry-etching, low-damage-plasma-ashing, and wet-cleaning processes after lithography with a test-element-group mask for 65-nm technology node. Wafers were then exposed to Ar discharge plasma in an attempt to seal pores on the trench sidewalls of the porous low-k films of the type A and B. A schematic of the sample structure is shown in Fig. 2.

Schematic diagram of an adsorption *in-situ* spectroscopic measurement setup is shown in Fig. 3. The stainless-steel vacuum chamber was equipped with a turbo-molecular / dry pumping system, a sample stage for a 300 mm silicon wafer, a load-lock chamber, a vapor supplying system, and a rotating-compensator-type *in-situ* spectroscopic ellipsometer whose probe light goes through the two ultraviolet-visible windows.

The ellipsometric spectra were measured at a light incidence angle of 70 degrees in the wavelength range of 300 – 800 nm during introduction and pumping down of the adsorptive vapor of *n*-heptane. Wafer temperature was maintained at 300 K during the measurement. The obtained spectra were analyzed with a two-layer optical model consisting of the capping and porous low-k layers on silicon substrate to monitor the changes in the optical properties of the porous low-k upon adsorption of the vapor adsorptive.

**Results and Discussion**
Experimentally obtained dependencies of refractive index $n$ and thickness $d$ of the porous low-k layer on adsorptive vapor pressure exhibited that $n$ increases with the *n*-heptane vapor pressure while $d$ stays almost constant. By converting the changes in $n$ and $d$ into the adsorbed amount of *n*-heptane according to the way which was reported earlier [1], we obtained adsorption / desorption isotherms, the results of which for the type B are shown in Fig. 4. Kelvin equation was then employed to calculate the pore diameter from the vapor pressure, and the *psd*s were obtained from the isotherm.

Figure 5 (a) and (b) show *psd*s of the patterned-wafer of type A and B, respectively, in which the results from the samples with and without Ar plasma treatment are compared. The obtained *psd*s for the patterned samples resembled those measured with blanket films (Fig. 1). It is also clear from Fig. 5 that the Ar plasma treatment does not affect *psd* significantly for the type-A sample with a larger pore size of 1.9 nm, but does very much for type B with a smaller pore size of 1.5 nm. It should be noted that the adsorptive molecule does not penetrate into the film through the capping layer, so that the experimentally observed apparent reduction in open porosity of sample B by about 40 % can be interpreted in terms of Ar-plasma induced pore sealing on the trench sidewall of the type-B porous low-k film. On the other hand, the Ar plasma treatment is not effective to pore-seal the sample A with a larger pore size.

## Conclusion

We have demonstrated characterization of pore sealing on trench sidewall by adsorption *in-situ* spectroscopic ellipsometry measurements of the patterned cap / low-k structures on silicon. Type B sample with a smaller pore size of 1.5 nm was pore sealed by Ar plasma treatment as much as 40 % in terms of *n*-heptane intrusion.


## Acknowledgments

This work was partly supported by New Energy and Industrial Technology Development Organization (NEDO). Japan Science and Technology Agency (JST) is acknowledged for Cooperative System for Supporting Priority Research.



## References

[1] C. Negoro, N. Hata, K. Yamada, and T. Kikkawa, Jpn. J. Appl. Phys. 43, 1327 (2004).


Table I Refractive index (*n*), density (ρ) and dielectric constant (*k*) of the two kinds of porous-MSQ samples used in the experiment.

| Type | *n* | ρ (g cm$^{-3}$) | *k* |
|---|---|---|---|
| A | 1.28 | 1.0 | 2.3 |
| B | 1.31 | 1.1 | 2.4 |

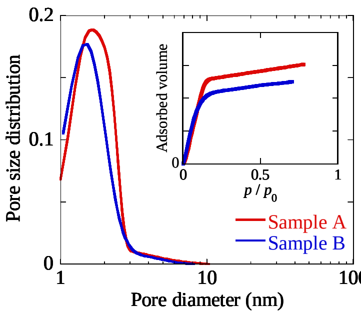


Fig. 1 Pore size distributions of the films.

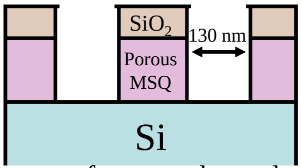


Fig. 2 Structure of patterned sample.

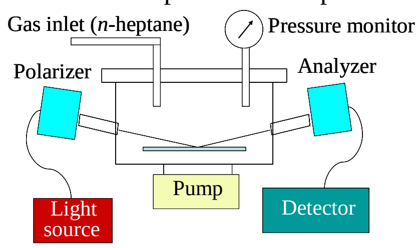


Fig. 3 A schematic diagram of *in-situ* ellipsometry measurement system.

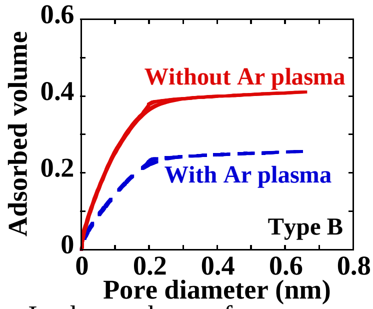


Fig. 4 Isotherm change for a patterned type B sample with Ar plasma treatment.

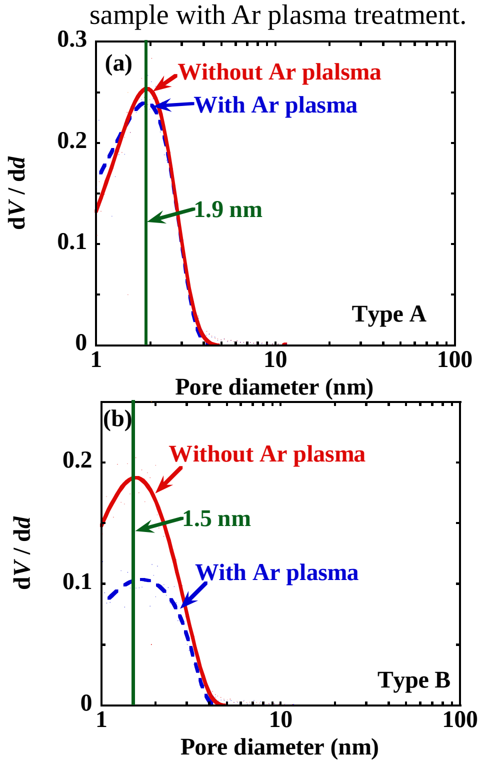


Fig. 5 Pore size distributions before and after Ar plasma treatment of patterned wafer, type A (a) and B (b) samples.