

Stiffening and hydrophilisation of SOG low- k material studied by ellipsometric porosimetry, UV ellipsometry and laser-induced surface acoustic waves

A. M. Urbanowicz¹, B. Meshman², D. Schneider³, and M. R. Baklanov¹

¹ IMEC, Leuven, Belgium

² IRSET, San Jose, USA

³ Fraunhofer Institute for Materials and Beam Technology, Dresden, Germany

Received 7 June 2007, accepted 20 November 2007

Published online 20 March 2008

PACS 43.35.Pt, 61.80.Ba, 61.82.Pv, 77.55.+f, 78.20.Ci, 78.66.Qn

In this paper we evaluate the correlation between UV light absorption of SOG (spin-on glass) low dielectric constant (low- k) films and chemical changes induced by an excimer UV source at several wavelengths: 172 nm, 222 nm, and 308 nm. Low- k absorption in the UV range was measured by nitrogen purged UV ellipsometry. It is shown that im-

provement of mechanical properties is accompanied by degradation (hydrophilisation) of low- k films. Changes in hydrophobic properties were evaluated by water-source ellipsometric porosimetry (WEP). The Young's moduli of the films were measured by laser-induced surface acoustic waves (LAwaves).

phys. stat. sol. (a) 205, No. 4, 829–832 (2008) / DOI 10.1002/pssa.200777749

Stiffening and hydrophilisation of SOG low- k material studied by ellipsometric porosimetry, UV ellipsometry and laser-induced surface acoustic waves

A. M. Urbanowicz^{*1}, B. Meshman², D. Schneider³, and M. R. Baklanov¹

¹ IMEC, Leuven, Belgium

² IRSET, San Jose, USA

³ Fraunhofer Institute for Materials and Beam Technology, Dresden, Germany

Received 7 June 2007, accepted 20 November 2007

Published online 20 March 2008

PACS 43.35.Pt, 61.80.Ba, 61.82.Pv, 77.55.+f, 78.20.Ci, 78.66.Qn

* Corresponding author: e-mail urbano@imec.be, Phone: +32 1628 1469, Fax: +32 1628 1214

In this paper we evaluate the correlation between UV light absorption of SOG (spin-on glass) low dielectric constant (low- k) films and chemical changes induced by an excimer UV source at several wavelengths: 172 nm, 222 nm, and 308 nm. Low- k absorption in the UV range was measured by nitrogen purged UV ellipsometry. It is shown that im-

provement of mechanical properties is accompanied by degradation (hydrophilisation) of low- k films. Changes in hydrophobic properties were evaluated by water-source ellipsometric porosimetry (WEP). The Young's moduli of the films were measured by laser-induced surface acoustic waves (LAwaves).

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Integration of low- k materials is a continuing issue in the microelectronics industry. To reduce the RC delay and improve the operating speed of multilevel Cu interconnects in modern ultra large scale integrated (ULSI) circuits, the k -value of dielectric layers has to be as low as possible. To decrease the k -value, porosity has been implemented to a new generation of dielectrics [1]. However, porous low- k materials have lower mechanical strength compared to conventional dielectric films. Improving mechanical properties (such as Young modulus) of new low- k materials becomes a challenge. The low- k dielectrics UV curing processes could solve this issue. The combined action of UV radiation and thermal activation is shown to generate a rearrangement in the bonding structure of the SiCOH based low- k [2]. As a result, the mechanical properties are improved, but the hydrophilicity increases. Subsequent moisture absorption into the porous structure significantly increases the k -value of dielectric film because of high polarizability of water molecules.

Most of results of low- k dielectrics UV curing reported so far are related to wideband UV sources. It is expected

that narrow band UV sources are more efficient for understanding of precise mechanisms of modification and such data are important for optimisation of technological processes. Optical transmission measurements of SiCOH based layers showing transparency in the far UV range with increasing absorption in the VUV suggest the use of excimer light source. The main advantage of an excimer light source is that it can emit light with very narrow spectral distribution.

In this paper we analyse the effect of UV and VUV excimer light of different wavelengths (172 nm, 222 nm and 308 nm), different power and exposure time to study a mechanism of photo induced changes of SOG low- k . The original (pristine) and UV treated SOG low- k films were characterized by nitrogen-purged ultra-violet (PUV) ellipsometry for determination of absorption in the UV range, ellipsometric porosimetry (EP) for determination of porosity and pore size [3], and ellipsometric porosimetry with water source (WEP) for evaluation of hydrophobic properties [4]. The mechanical properties of the films were evaluated by laser-induced acoustic wave spectroscopy

(LAwave) [5]. Fourier transform infrared (FTIR) spectroscopy was used for characterisation of the chemical composition before and after UV irradiation.

2 Experimental

2.1 Samples preparation The samples used in this study were silica-based low-*k* films deposited on 200 mm silicon wafers by SOG technology. The films had 10–12% carbon-containing-hydrophobic groups, 32% porosity, and a pore size close to 2 nm after a standard curing (thermal annealing). The *k*-value of the films was in the range of 2.3–2.4. Such prepared samples were irradiated by plasma-based, planar VUV (vacuum ultra-violet) source, which provides single or multiple bands between 120 nm and 350 nm (Fig. 1). For this evaluation, 172 nm, 222 nm and 308 nm were used. The plasma is induced in a chamber with excimer gas mixture. The light from the plasma is emitted into processing chamber through a special quartz window. The spectral distribution of the emitted light depends on excimer gas composition as shown in Fig. 2. During the UV exposure, the sample chamber is flowing with N₂ (99.99% purity) and continuously pumped down. N₂ pressure is about 1 Torr with flow 0.1 liter per minute.

2.2 Metrology The refractive index and extinction coefficient of the film studied were measured by a Sopra PUV-EP ellipsometric system ($\lambda = 150\text{--}650\text{ nm}$). Measurements were done in nitrogen ambient at atmospheric pressure. Amount of H₂O and O₂ during measurement was below the level of 5 ppm. Porosity, pore size distribution and bulk hydrophilicity were measured by using ellipsometric porosimeter EP-10 equipped with SENTECH 801 spectroscopic ellipsometer ($\lambda = 350\text{--}850\text{ nm}$). The ellipsometer is mounted on a vacuum chamber that can be filled with a solvent vapor (such as toluene or water) in a controllable way [3, 4].

The elastic modulus of the films studied were measured by LAwave. This technique is based on high frequency surface acoustic waves, which are very sensitive to surface film, even if their thickness is much thinner than the penetration depth of the waves. The acoustic waves are generated by a short laser pulse in a wide spectral range. The phase velocity of the wave propagation is measured depending on a frequency. Fitting the theoretical curve to

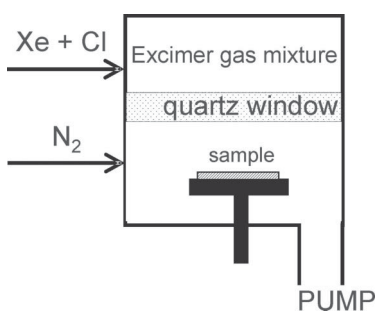


Figure 1 Scheme of the experimental setup.

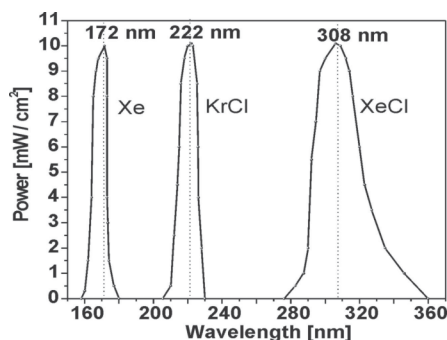


Figure 2 Power versus wavelength of emitted light for different excimer mixtures.

the curve measured yields the elastic modulus (Young's modulus) of the film [5].

The chemical composition of low-*k* films before and after UV irradiation was analyzed using a Biorad QS2200 ME FTIR system.

3 Results and discussion Figure 3 shows the refractive index and the extinction coefficient of the pristine low-*k* dielectric film (no UV treatment) in a range from 150 nm to 650 nm. The pristine sample has strong absorption below 180 nm. It indicates that the UV region below 180 nm is photochemically active according to a fundamental law of photochemistry [6]. Figure 4 reflects changes of Young moduli (YM) after UV irradiation. The *y*-axis presents exposure. The exposure is product of UV power, time of treatment and light frequency. The highest changes in YM are observed for 172 nm. This improvement of mechanical properties indicates that wavelength of light below 180 nm causes the highest efficiency of photochemical reactions. Dielectric films treated with 222 nm and 308 nm UV reveals small improvement of YM. This correlates well with FTIR and EP data as presented in Figs. 5 and 6.

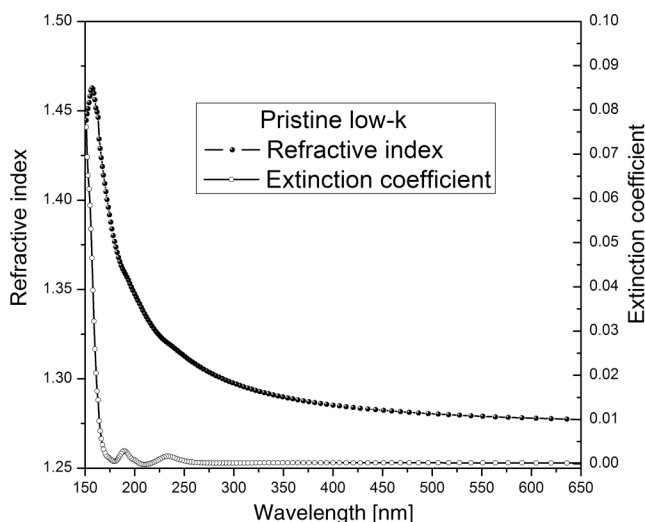


Figure 3 Refractive index and extinction coefficient of the low-*k* (as measured by PUV) versus wavelength.

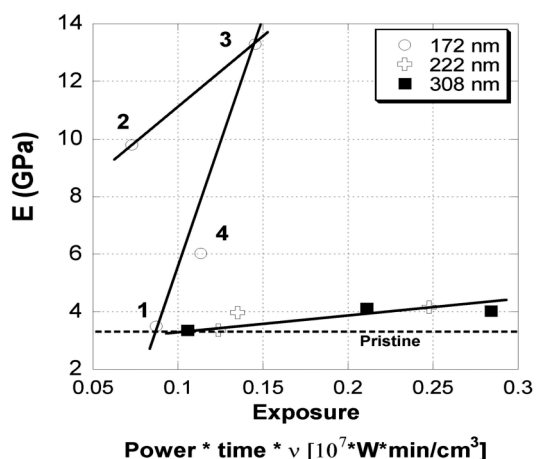


Figure 4 Young's moduli (as measured by LAwave) versus UV exposure. The numbers on the graph correspond to the sample numbers in Table 2.

Figure 5 shows ratio Si–O–Si (1050 cm^{-1}) cage bond to Si–CH₃ (1276 cm^{-1}) FTIR peaks versus exposure. This ratio reflects well the compromise between hydrophilicity and mechanical properties. Increasing the number of Si–O–Si groups gives better mechanical properties. While the number of Si–O–Si groups increases, a reduction of the number of CH₃ (methyl) groups is observed [7]. The methyl groups are hydrophobic due to low polarizability. Depletion of CH₃ groups leads to hydrophilisation of the low-*k*. The degree of hydrophilisation is shown in Fig. 6. The hydrophilisation of UV treated low-*k*'s can be related to photo-dissociation of carbon containing groups and a cross-linking mechanism of the Si–O–Si network. Possible reactions for UV and VUV irradiation are presented in Table 1.

Another reason of hydrophilisation can be related to influence of residual oxygen in the UV vacuum chamber. Excited oxygen can remove carbon-containing hydrophobic groups.

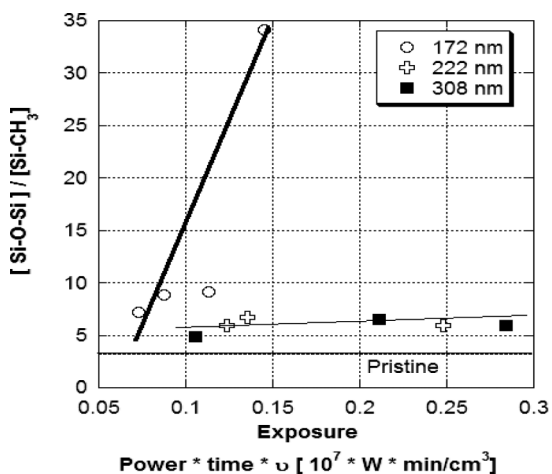


Figure 5 Si–O–Si/Si–CH₃ ratios (as measured by FTIR) versus exposure.

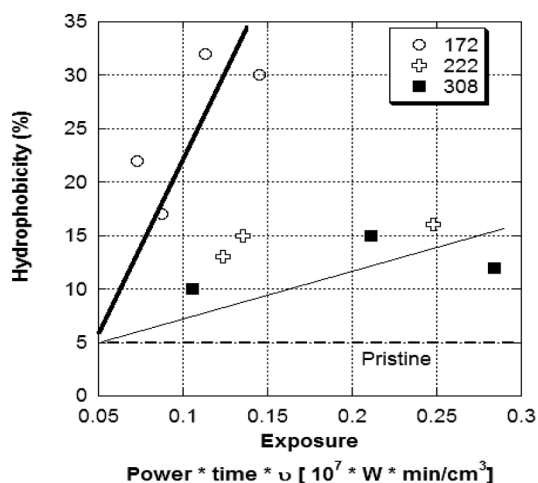


Figure 6 Hydrophilicity (as measured by EPW) versus exposure.

The energies of the reactions listed in Table 1 were calculated by Ushio et al. who used molecular models of the reactants and products and a first-principles molecular orbital program, Gaussian 03 [8]. Since the reaction energy corresponds to the driving force of a reaction in a thermodynamic sense, reactions 1 and 2 are the most probable to occur. Reaction 4 is insignificant, because the reaction energy is negligible. Considering the reaction energies and comparing the changes in measured FTIR spectra, we can conclude that a Si–O–Si cross-link generation from a CH₃ group and OH group is the primary reaction. Methane (CH₄) releases as a reaction product of this reaction. Therefore, Si–O–Si cross-link generation leads to CH₃ groups depletion and, as a result, strong hydrophilisation occurs.

The results of our tests and settings of the UV system are summarized in Table 2. These data show that the highest modification of low-*k* films occurs after 172 nm irradiation due to strong absorption of our material in this region (Fig. 3). This correlates with a reduction of porosity and a mean pore radius (as measured by EP). Moreover the ratio Si–O/Si–CH₃ (as calculated from FTIR) reflects that improvement of mechanical properties leads to reduction of the number of hydrophobic CH₃ groups. This correlates with WEP data. Mechanical properties are improved but hydrophobic properties become significantly worse. In the region of 200–400 nm the impact of photochemical reac-

Table 1 Possible reactions during UV and VUV irradiation and their reaction energies (i.e., differences between energies of reactants and those of products) [2].

reaction	energy [eV]
1 $\text{O}_3\text{Si}-\text{CH}_3 + \text{HO}-\text{SiO}_3 \rightarrow \text{O}_3\text{Si}-\text{O}-\text{SiO}_3 + \text{CH}_4$	1.64
2 $\text{O}_3\text{Si}-\text{H} + \text{HO}-\text{SiO}_3 \rightarrow \text{O}_3\text{Si}-\text{O}-\text{SiO}_3 + \text{H}_2$	1.43
3 $\text{O}_3\text{Si}-\text{CH}_3 + \text{H}_2 \rightarrow \text{O}_3\text{Si}-\text{H} + \text{CH}_4$	0.21
4 $\text{O}_3\text{Si}-\text{OH} + \text{HO}-\text{SiO}_3 \rightarrow \text{O}_3\text{Si}-\text{O}-\text{SiO}_3 + \text{H}_2\text{O}$	0.12

Table 2 Summary of experimental conditions and results.

sample	wavelength (nm)	time (min)	power	FTIR Si–O/Si–CH ₃	EP pore radii (nm)	EP porosity (%)	EPW water (%)
1	172	10	low	8.90	0.80	32	17
2	172	5	med	7.24	0.75	26	22
3	172	10	med	34.14	0.60	27	30
4	172	3	high	9.15	0.60	32	32
5	222	10	low	6.68	0.85	33	15
6	222	5	high	5.90	0.90	33	13
7	222	10	high	5.94	0.80	32	16
8	308	5	low	4.83	0.90	32	10
9	308	10	low	6.52	0.80	34	15
10	308	5	high	5.94	0.90	31	12
11	pristine	–	–	4.61	1.00	32	5

tions is low because of low low-*k* absorption. However, we still observed some changes after 222 nm and 308 nm UV irradiation. We can assume that it may be related to “hot plate nature”. When a sample is irradiated with UV wavelength from “hot plate” region, most of the light is transmitted through low-*k* and warms up the Si substrate due to strong absorption of silicon for the wavelengths shorter than 400 nm. This effect could be related to multi-photon absorption on the Si substrate near interlayer with the low-*k*. Temperature of the Si substrate may play a role in physical and chemical processes occurring during the UV treatment of the low-*k*.

4 Conclusions The largest improvement of the mechanical properties of the low-*k* studied occurs during 172 nm UV irradiation due to the fact that the absorption edge of the SOG low-*k* matrix lies below 180 nm. However, improving the mechanical properties of low-*k* films by UV light leads to significant hydrophilisation. This phenomenon is related to removing of hydrophobic carbon-containing groups as a result of UV induced photo-dissociation and Si–O–Si cross-linking mechanism. The degree of hydrophilisation of 172 nm was higher than in the case of 222 nm and 308 nm. There are two possible reasons. One reason could be related to the smaller degree of photo-chemical reactions due to lower UV light absorption for 222 nm and 308 nm wavelengths. Another reason might be related to influence of residual oxygen in UV

vacuum chamber which could be excited by 172 nm radiation. Therefore, an optimal balance between improvement of mechanical properties and hydrophilisation of a low-*k* must be established.

Acknowledgement It is our pleasure to thank Dennis Shamiryan for fruitful discussions.

References

- [1] K. Maex, M. R. Baklanov, D. Shamiryan, F. Iacopi, S. H. Brogersma, and Z. S. Yanovitskaya, *J. Appl. Phys.* **93**(11), 8793 (2003).
- [2] J. Ushio, T. Ohno, T. Hamada, S.-I. Nakao, K. Yoneda, M. Kato, and N. Kobayashi, *Jpn. J. Appl. Phys.* **46**, 17 (2007).
- [3] M. R. Baklanov and K. P. Mogilnikov, *Microelectron. Eng.* **64**, 335 (2002).
- [4] M. R. Baklanov, K. P. Mogilnikov, and Q. T. Le, *Microelectron. Eng.* **83**, 2287 (2006).
- [5] D. Schneider, P. Siemroth, T. Schülke, J. Berthold, B. Schultrich, H. H. Schneider, R. Ohr, B. Petereit, and H. Hilgers, *Surf. Coat. Technol.* **153**, 252 (2002).
- [6] J. G. Calvert and J. N. Pitts, *Photochemistry* (Wiley, New York, 1967), pp. 10–50.
- [7] K. Yoneda, M. Kato, N. Kobayashi, N. Matsuki, K. Matsushita, N. Ohara, A. Fukazawa, and T. Kiura, *Proc. 2005 Interconnect Technology Conf.*, p. 220.
- [8] M. J. Frisch et al., *Gaussian 03* (Gaussian, Inc., Wallingford, CT, 2004), Revision B.05.