



PERGAMON

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Radiation Physics and Chemistry 68 (2003) 345–349

Radiation Physics
and
Chemistry

www.elsevier.com/locate/radphyschem

Characterizing porosity in nanoporous thin films using positronium annihilation lifetime spectroscopy

J.N. Sun, Y.F. Hu, W.E. Frieze, D.W. Gidley*

Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA

Abstract

Depth profiled positronium annihilation lifetime spectroscopy (PALS) is an extremely useful probe of the pore characteristics of nanoporous thin films in general and low-dielectric constant (k) thin films in particular. PALS is sensitive to all pores (both closed and open) in the size range from 0.3 to ~ 300 nm and to the closed-to-open pore transition. Deduced pore sizes have been extensively compared with other techniques in an ongoing round-robin with other laboratories. The application of PALS in issues related to Cu/low- k film microchip integration will be demonstrated.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: PALS; Porous films; Low- k dielectric films

1. Introduction

Porosity control is an important aspect of the emerging field of nanoengineering. Introducing engineered porosity into microelectronic materials such as low- k dielectric films, into biotechnology films such as bio-membranes and polymeric selective permeation filters, and into chemical systems such as catalytic films is attracting intense research interest. As a specific example of the broadly applicable positronium annihilation lifetime spectroscopy (PALS) technique we focus herein on the extensive efforts to develop low- k materials in order to reduce the resistance–capacitance delay in integrated circuits (IC). According to the 1999 International Technology Roadmaps of Semiconductors, incorporating nanoporosity is required to produce ultra low- k films ($k < 2.2$) as the feature size of IC's shrink below $0.10 \mu\text{m}$. Understanding the pore structure, such as pore size, distribution, and pore interconnectivity in porous low- k films is crucial since these parameters are fundamentally important in determining electrical and mechanical properties. Unfortunately, there are relatively few techniques capable of probing nanometer-

sized pore characteristics in sub-micron films on thick substrates. Beam-based PALS (Gidley et al., 1999, 2000a; Petkov et al., 2000) has recently been demonstrated to be powerful in determining interconnected and/or closed porous structure in low- k films and beam-based Doppler broadening positron annihilation spectroscopy (Petkov et al., 1999) has been used to probe void volume and pore interconnectivity. In this paper we will review the methodology of PALS in exploring the pore characteristics (size, distribution, and interconnectivity) in thin (sub-micron), porous low- k films. A model calibration that relates positronium annihilation lifetime with pore size has been developed and a recent round-robin comparison with other pore characterization techniques in various low- k films will be presented. PALS has also been used to investigate diffusion barrier integrity and the structural changes of porous low- k films during their integration with Cu.

2. PALS experimental technique

In using PALS with thin films, an electrostatically focused beam of several keV positrons generated in a high vacuum system is implanted into the sample. The

*Corresponding author. Fax: +1-734-764-5153.

E-mail address: gidley@umich.edu (D.W. Gidley).

positron slows down through collisions in the material from its initial beam energy of several keV to several eV. It can either capture a bound molecular electron or recombine with free “spur” electrons generated by ionizing collisions to form the electron–positron bound state of positronium, Ps. This Ps, which initially has a few eV of kinetic energy, begins to diffuse and thermalize in the insulator. In porous films it localizes in the void volume where its natural annihilation lifetime of 142 ns is reduced by annihilation with molecular electrons during collisions with the pore surface. The collisionally reduced Ps lifetime is correlated with void size and forms the basis of the technique.

Ps may diffuse over long distances that can be greater than the porous film thickness if the pores are interconnected (Gidley et al., 1999, 2000b). As a result Ps can easily diffuse out of the film and into the surrounding vacuum. The observable effect on the Ps lifetime is that most of the Ps annihilates with the vacuum lifetime of 142 ns, a telltale indicator that the pores in the film are interconnected. To extract information on the average pore size (technically, the mean free path for Ps in the interconnected pores) it is necessary to deposit a thin capping layer on top of the film to keep the Ps corralled in the porous film (Gidley et al., 1999). Once the film is capped, a single lifetime component corresponding to the average mean free path of Ps throughout the entire porous network is fitted. If the pores are closed then Ps should be trapped in a pore with no further diffusion occurring. Indeed, in such materials no capping layer is required. Furthermore, a distribution of Ps lifetimes may result if there is a distribution of pore sizes. A method to deconvolve a pore size distribution from a Ps lifetime distribution has been described by Gidley et al. (2000a).

3. Calibration of pore size

It is important to calibrate Ps lifetimes with pore sizes. In the very large pore (non-quantum mechanical “classical”) regime (pores with mean free paths of order 100 nm), calibration was performed using very high porosity (90–98%) silica powders. In the other extreme (sub-nm pores), the quantum mechanical model first developed by Tao (1972) and Eldrup et al. (1981) has been empirically used to calibrate Ps lifetimes of several nanoseconds with pore size, such as those in polymers. With only the ground state of Ps being considered in this Tao-Eldrup model, it is insufficient for characterizing larger voids where the pore diameter approaches the thermal De Broglie wavelength of positronium (about 6 nm). Thermally excited states of Ps atoms in the pore must be included in the calculation. As a result, the sample temperature should explicitly appear in the calibration of lifetime vs. pore size.

To fully extend the quantum mechanical model throughout the classical, large-pore limit, we have modified the Tao-Eldrup model (Dull et al., 2001). To summarize, a rectangular pore shape is assumed for calculational simplicity (to avoid high order Bessel functions) and it is assumed that there is no Ps-surface interaction. It is assumed that the Ps atoms randomly sample all of the states in the rectangular well with a probability governed by a Maxwell–Boltzman distribution. At a given sample temperature, a lifetime vs. pore dimension curve can be calculated. We have considered flat planes, long square channels, and cubic pores where Ps is localized in 1, 2 and 3 dimensions, respectively. It is useful to convert such curves from a model-specific pore dimension to a mean-free path, $l = 4V/S$, where V/S is the pore volume-to-surface area ratio. The mean-free path is a linear measure of pore size that is not specific to any pore geometry.

Fig. 1 shows Ps lifetime vs. mean-free path curves at several different temperatures. Cubic pores were used in the calculations. The model includes only one fitting parameter that is determined by existing experimental data for l below 2 nm. At room temperature, the model extrapolates perfectly through precision measurements in large-pore silica powders as shown. Direct temperature-dependent Ps lifetime measurements in heated porous silica are in good agreement with predictions (Dull et al., 2001; Gidley et al., 1999) and Ps time-of-flight energy spectroscopy shows that the emitted Ps into vacuum is highly thermalized. Thus the assumption of a Maxwell–Boltzman distribution of Ps excited states is entirely appropriate.

The extended Tao-Eldrup model not only agrees with data in the Tao-Eldrup (sub-nm) and classical large-pore

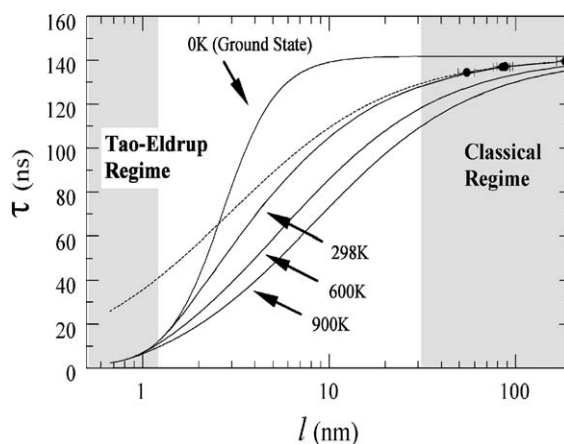


Fig. 1. Pore-size calibration calculated at different temperatures using a cubic pore model of side-length a . The mean free path is then $l = (\frac{4}{3})a$. The dashed curve is the extrapolation from a classical large-pore, wall collision rate calculation as discussed in Gidley et al. (1999).

regimes, but is also found to be valid in the intermediate, semi-classical regime. In fact, Ps lifetimes measured in bulk silica gels with pores calibrated by gas adsorption methods are in quite reasonable agreement with the room temperature curve (Dull et al., 2001 and references therein). Two years ago, a systematic round-robin of identical porous low- k thin films from different manufacturers was initiated to compare the results of beam-PALS, specular X-ray reflectivity (SXR)/small angle neutron scattering (SANS), traditional N_2 porosimetry (BET) and ellipsometric porosimetry (EP). Results are determined independently and not disclosed between the participants before any comparison is made. The low- k films studied are made from a variety of materials such as silica, silsesquioxane, and polymers from different processing methods. All these films are determined to have interconnected, open pores and hence have been capped for PALS analysis. These data are plotted in Fig. 2, focusing on comparing PALS with other techniques directly. In this figure, PALS measurements utilize a two-dimensional, infinitely long, square channel pore model (where the mean free path is the channel length and can therefore be thought of as the diameter of a cylindrical pore). In the pore “diameter” range from 2 to 15 nm, reasonable (not perfect) agreement in open pore size measurement is observed. These comparisons suggest that our rectangular extension of the Tao-Eldrup model is valid and accurate for a range of materials. It is applicable to any size pores at any sample temperature. Indeed, the great strength of PALS may be in its sensitivity to both open and closed pores, even if they are hidden beneath a diffusion barrier layer.

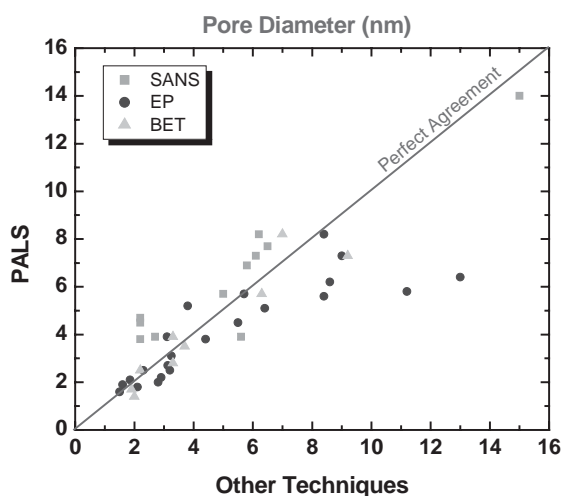


Fig. 2. Comparison of PALS pore-size measurements with other methods. The four EP points lying farthest to the right of the line are all from one film set having bi-model pore distributions and are under further scrutiny.

4. Pore percolation

It is straightforward using PALS to distinguish between open (interconnected) and closed pore structure based on the intensity of the Ps signal in vacuum. In interconnected pores, the highly mobile Ps atoms readily escape into vacuum while only backscattered Ps in vacuum can be observed from closed pore films. This allows one to determine the evolution of pore structures and the transition from closed-to-open pores, defined as “percolation threshold” (Petkov et al., 2000; Sun et al., 2002a).

To illustrate how one might use PALS to routinely determine pore percolation parameters we have depth-profiled a set of porous silsesquioxane low- k films and the results are presented in Fig. 3. At each beam energy Ps increasingly escapes into vacuum as the porogen loading is increased. Despite probing deeper into the film with higher positron beam implantation energy, all the plots consistently extrapolate to zero Ps escape intensity at $\sim 11\%$, the deduced percolation threshold for this film’s particular material and fabrication processing. We could clearly simplify future determinations of the percolation threshold by using only one beam implantation energy. Moreover, depth-profiling PALS can determine the percolation length, the length scale over which pores are interconnected for each film as described by Sun et al. (2002a). This is defined to be the Ps diffusion length for films just above percolation threshold where Ps diffusion is clearly frustrated by limited interconnectivity of the pores.

5. Diffusion barrier integrity

Advanced devices will require integration of low- k films with Cu. A simple method to directly probe the

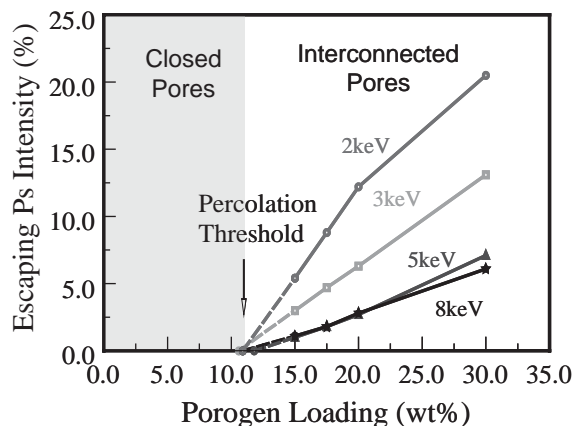


Fig. 3. A consistent percolation threshold of 11% is deduced from extrapolation at four different positron beam implantation energies.

continuity of diffusion barrier layers between Cu and open-pored low- k films is illustrated in Fig. 4. Positrons are injected into the dielectric film and form Ps that diffuses rapidly throughout the interconnected pores. Despite many collisions with the barrier, a continuous overlayer should prevent Ps from escaping into vacuum. Hence, detection of Ps in vacuum through its telltale 140 ns vacuum lifetime clearly indicates leakage through pinholes or discontinuities in the barrier. In collaboration with International Sematech, we have performed a systematic test of the integrity of Ta and TaN diffusion barriers as described by Sun et al. (2001). Minimum barrier layer thickness is determined based on the Ps vacuum intensity signal. The results are substantiated by transmission electron microscope (TEM) analysis of the barrier structure. PALS on patterned samples are no more difficult to perform than on the blanket films used in this study. The feasibility of PALS in testing barrier thermal stability has also been reported. The technique is sensitive to both process-induced and thermally activated barrier interdiffusion (contamination) of the porous structure, as clearly signaled by the drastically reduced Ps lifetime (Sun et al., 2001). Here was a situation where a TaN layer was still a continuous barrier (as evidenced by no escaping Ps into vacuum), however, a thermal treatment-induced reduction in Ps lifetime in the mesopores indicates unacceptable contamination of the dielectric.

6. Integration-induced densification

Promising porous low- k thin films will inevitably be exposed to reactive plasmas used in the integration process with Cu, such as for capping, etching and ashing processes. The porous structure and the low mechanical strength bring up concerns about the stability and integrity of the low- k films. PALS has been demon-

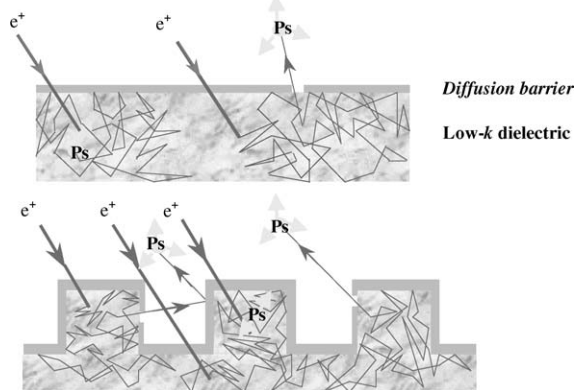


Fig. 4. An illustration of Ps diffusion barrier testing in blanket and patterned (trenched) samples prior to any Cu deposition.

strated to be a valuable technique for probing the integration damage of interconnected porous networks of low- k thin films (Sun et al., 2002b). For instance, specimens of a porous film were exposed to different plasma treatments for various lengths of time. Depth-profiling PALS observed no Ps leakage signal into vacuum in all of the processed films, as shown in Fig. 5 (top), indicating that a dense top layer was formed on all of the processed films. Ps mesoporous intensities (Fig. 5 bottom) were found to decrease with increasing exposure time to the plasma, indicating that this densified layer grows deeper into the highly interconnected porosity as the plasma treatment time becomes longer. In the extreme case of O₂ ashing there appears to be complete collapse of all the pores. It is interesting to note that in all cases the size of the remaining mesopores

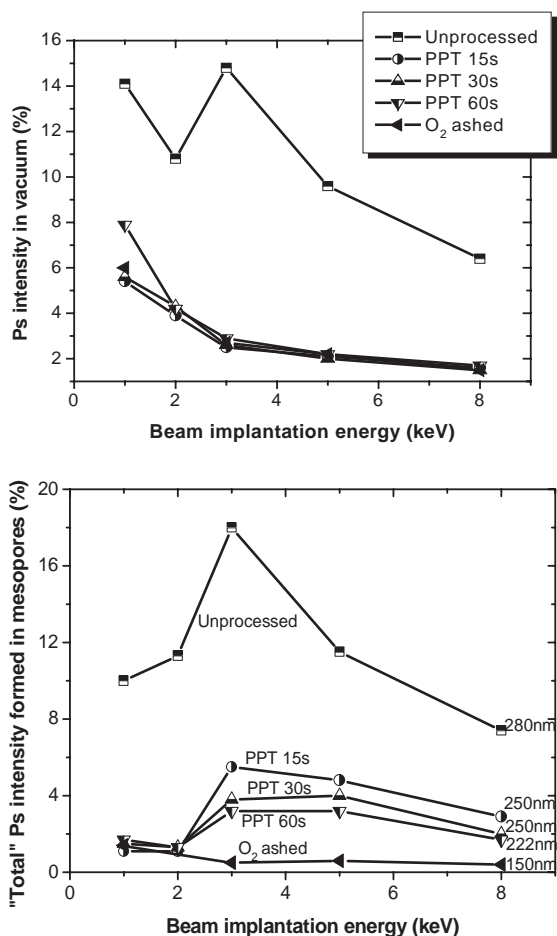


Fig. 5. Top: Ps vacuum intensity (only the Ps escaping into vacuum) in the plasma pre-treated (PPT) films. An unprocessed, open-pored film is included for comparison. Bottom: "Total" of all Ps formed in mesopores (includes Ps annihilating in the mesopores as well as in vacuum). Film thicknesses on the right, determined using a scanning electron microscope, indicate film shrinkage has occurred.

underneath this layer is found to be unchanged. The capability to detect the pore structure evolution underneath a dense layer, a unique feature of PALS, further demonstrates that PALS remains powerful even in exploring integration-induced densification.

7. Conclusion

Advances in nanoscale science and engineering will require advances in the technology of thin film porosity characterization. Traditional probes are severely challenged by the often amorphous nature of these films and by the nanoscale size of the pores. Positron researchers have exploited for some three decades the sub-nanometer sensitivity of PALS to voids and defects in bulk materials. Depth-profiled *beam* PALS then enabled thin insulating film studies (Xie et al., 1995). However, the sharp upturn in interest in positron annihilation spectroscopies is, in our opinion, a result of demands in nanotechnology for porous thin amorphous films with small pore sizes less than 10 nm. Engineered nanoporosity in microelectronic, low-*k* thin films is a perfect example of such an emerging need in nanotechnology. Beam PALS as a non-invasive, non-destructive probe of nanopore characteristics is ideally suited to meet present and future needs in this area. Future engineered pore sizes will not challenge PALS small-pore sensitivity, nor will films become too thin (<10 nm) for PALS analysis. Moreover, our experience to date with the low-*k* film round-robin indicates that the PALS pore-size calibration is equal to, if not systematically more reliable than, other techniques (especially for pore diameters <5 nm). However, the clear distinction that PALS makes between closed and interconnected porosity is not borne out by other techniques that rely on solvent or gas absorption. Clearly, Ps will not move atoms that block its diffusion in the manner that an impregnating solvent or gas atom could clear a path, or even swell the film. Closer systematic comparisons are underway on this issue. Perhaps the most important shortcoming of the PALS technique is that we do not yet know how to deduce a measurement of absolute porosity without independent calibration (relative porosity, on the other hand, appears completely consistent in comparative studies). This may require a more intimate knowledge of the Ps formation mechanism coupled with knowledge of

the Ps diffusion length in the dense medium. With continued work on this issue and further testing of the large pore calibration of PALS the future looks bright for the role of positron spectroscopies in characterizing nanoporous materials for the highly topical nanotechnology initiative.

Acknowledgements

We thank all our collaborators at International Sematech, NIST, Dow Corning, AMD, Nanopore, Shipley, Lucent, Intel, Samsung, IMEC (Belgium), Institute of Materials Research and Engineering (IMRE-Singapore), and Seoul National University for their continuing interaction and support. This research at the University of Michigan is supported by NSF grant ECS-0100009, the Low-*k* Dielectric Program at International Sematech, and IMRE.

References

- Dull, T.L., Frieze, W.E., Gidley, D.W., Sun, J.N., Yee, A.F., 2001. *J. Phys. Chem. B* 105, 4657.
- Eldrup, M., Lighbody, D., Sherwood, J.N., 1981. *Chem. Phys.* 63, 51.
- Gidley, D.W., Frieze, W.E., Yee, A.F., Dull, T.L., Ho, H.-M., Ryan, E.T., 1999. *Phys. Rev. B, Rapid Comm.* 60, R5157.
- Gidley, D.W., Frieze, W.E., Dull, T.L., Sun, J., Yee, A.F., Nguyen, C.V., Yoon, D.Y., 2000a. *Appl. Phys. Lett.* 76, 1282.
- Gidley, D.W., Frieze, W.E., Dull, T.L., Sun, J., Yee, A.F., 2000b. *Mater. Res. Soc. Symp. Proc.* 612, D.4.3.1.
- Petkov, M.P., Weber, M.H., Lynn, K.G., Rodbell, K.P., Cohen, S.A., 1999. *J. Appl. Phys.* 86, 3104.
- Petkov, M., Weber, M., Lynn, K.G., Rodbell, K., 2000. *Appl. Phys. Lett.* 77, 2470.
- Sun, J.N., Gidley, D.W., Dull, T.L., Frieze, W.E., Yee, A.F., Ryan, E.T., Lin, S., Wetzels, J., 2001. *J. Appl. Phys.* 89, 5138.
- Sun, J.N., Gidley, D.W., Hu, Y.F., Frieze, W.E., Yang, S., 2002a. *Mater. Res. Soc. Symp. Proc.* 726, Q 10.5.
- Sun, J.N., Gidley, D.W., Hu, Y.F., Frieze, W.E., Ryan, E.T., 2002b. *Appl. Phys. Lett.* 81, 1447.
- Tao, S.J., 1972. *J. Chem. Phys.* 56, 5499.
- Xie, L., DeMaggio, G.B., Frieze, W.E., DeVries, J., Gidley, D.W., Hristov, H.A., Yee, A.F., 1995. *Phys. Rev. Lett.* 74, 947.