Measuring the continuity of diffusion barriers on porous films using γ-ray energy spectra of escaping positronium

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Diffusion barriers for capping porous low dielectric constant films are important for preventing metal migration into a semiconductor circuit. Using the fact that positrons implanted into a porous dielectric form ortho-positronium (o-Ps) copiously, Gidley *et al.* [D. W. Gidley, W. F. Frieze, T. L. Dull, J. Sun, A. F. Yee, C. V. Nguyen, and D. Y. Yoon, Appl. Phys. Lett. **76**, 1282 (2000)], have been able to measure open area fractions as low as 10^{-5} in porous dielectric film barrier layers from the increase in the ortho-positronium lifetime and intensity associated with positronium escape into vacuum. We demonstrate that it is possible to obtain comparable sensitivities by measuring the gamma-ray energy spectrum of the escaping positronium. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2007862]

Cap layers on porous films are of interest in controlling the gas permeability of nanoporous membranes,[1] for detecting biological single molecules,[2] and preventing diffusion of contaminants into ultra low-k dielectric materials used in semiconductor interconnects.[3,4] Nanopores inside a dielectric film supporting the on-chip wiring of an integrated circuit can reduce the film's dielectric constant to less than 2 from the current value of about 4 for SiO_2, with a proportional decrease in the signal propagation delays and a concomitant increase in computing speeds due to the reduced RC time constants. However, porous low-k dielectric films are produced in a way that results in the pores being interconnected and this presents a technical obstacle to their utilization as interlayer dielectrics (ILDs).[3,4] The problem is that atoms of the most desirable electrode material, copper, can diffuse into the dielectrics through the connected pores, resulting in serious device degradation. It is therefore necessary to have a thin barrier layer to separate the metal interconnect lines from the surrounding ILD. While it might be desirable to have a nondestructive way of monitoring barrier characteristics during production, most studies to date involve measurements of the degradation of electrical properties after a barrier has been integrated into an electrically active device.

A nondestructive method for sampling the continuity of thin barrier layers involves the use of positronium (Ps), the lightest hydrogen-like atom consisting of a bound electron-positron pair. It is assumed that if a small atom like positronium cannot escape through a thin barrier, then large metallic atoms most likely cannot diffuse through the barrier either. Taking advantage of the fact that positronium is formed with high probability when positrons are implanted into porous dielectric films, Gidley and co-workers have used the probability of positronium escaping from a film into vacuum to detect the presence of discontinuities in barrier layers using positron annihilation lifetime spectroscopy.[5] The signal that Ps has escaped through a barrier is the amplitude of a lifetime component corresponding to the ortho-positronium (o-Ps) lifetime in vacuum, 142 ns, easily distinguished from the 10–100 ns o-Ps lifetime in the film. The method of Gidley *et al.* is surprisingly sensitive to the open area fraction of a barrier layer because of the high velocity of Ps at room temperature and its relatively long lifetime in the porous material. We demonstrate that one may also achieve quantitative parts-per-million sensitivity for probing the continuity of diffusion barriers on porous films using depth profiles based on various positron annihilation gamma ray spectroscopy signals (the 3γ annihilation fraction of ortho-positronium and the 2γ annihilation line shape or S parameter) as well as the positronium annihilation lifetimes.

Samples of caped porous silica films, Nanoglass (MTAS / A10) (400 nm thick), on a silicon substrate were supplied by Lucent Technologies. The porous silica films were formed by tetraethylorthosilicate polymerization with silica and subsequent decomposition of the organic template. The decomposition creates pores after the silica matrix is fully cured and cross linked. Nanoglass films were capped with Ta barrier materials using a physical vapor deposition method at room temperature and annealed below 300 °C. A porous methylsilsesquioxane (MSQ) film having no barrier and prepared using a sacrificial triblock copolymer F88 (Ref. 6) is used for comparison.

When positrons are injected into a highly interconnected porous layer, both para-positronium (p-Ps) and ortho-positronium (o-Ps) are formed. If o-Ps escapes the cap layer, it emits 3γ photons outside of the film. The o-Ps inside the porous layer collides with the wall of the pores, mostly annihilating via 2γ emission, the probability of 3γ emission being the ratio of the 3γ annihilation rate in vacuum to the annihilation rate in the pores. Therefore, the 3γ emission probability mostly represents o-Ps escaping from the barrier.

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The p-Ps cannot move very far in a pore channel because it annihilates into 2γ very quickly (125 ps). For highly porous materials, 2γ annihilations mainly reflect p-Ps annihilation and the o-Ps pickoff annihilation processes, both of which occur inside the porous film.

Measurements of the photon energy spectra of annihilation radiation were conducted using a slow positron beam apparatus at Oak Ridge National Laboratory (ORNL). The beam starts with a 20 mCi ^{22}Na source, which emits positrons with energy of a few hundred keV. An argon film is condensed on a cold (4 K) finger and annealed at about 40 K for a few minutes. With this procedure, the fast positrons are moderated to yield a beam of 0.9×10^6 positrons/s which passes through an $E\times B$ filter and are guided to the target. The energy with which the positrons impinge upon the sample is varied from 30 eV to 30 keV by applying a negative voltage to the sample. A high-resolution, high-efficiency (80%) Ge detector is used for measuring the annihilation gamma spectra. The R parameter, which is sensitive to the $3\gamma/2\gamma$ ratio, was defined as the counting rate in the photon energy range 100–450 keV, divided by the counting rate in the 511 keV 2γ photopeak. The S parameter was measured by recording counts in the center area of the 511 keV peak divided by the total area of the peak and the W parameter was defined as the counts in the tail area of the peak divided by the total area. Positronium annihilation lifetime spectroscopy measurements were conducted using a pulsed positron beam at AIST, Japan. A detailed description can be found in Ref. 7.

Figure 1 shows the R parameter as a function of depth for various barriers on the porous silica films. The depth unit is expressed as the incident positron energy, which determines the mean depth approximately[8] by $d(\text{nm})=40E^{1.6}/\rho$, where d is the mean depth in nm; ρ is the density of the film in g/cm^3, and E is the positron implantation energy in keV. Since the log of the positron energy is a linear function of the log of the mean depth, the depth axis is plotted in log scale. The interfaces between the barrier layer, the porous silica layer, and the silicon substrate are identified in the figure using the above formula.

Figure 1(a) shows an R parameter profile for a porous MSQ film without any barrier. A large value of R was observed when positrons were injected into the porous film. Since most of the o-Ps 3γ emission occurred in vacuum, therefore such a large R value $R_{\text{Ps}}=0.725\pm0.007$ suggests that most of the o-Ps escaped from the surface. When positrons were injected into the silicon substrate, where there are no pores, o-Ps cannot be formed and thus the $3\gamma/2\gamma$ ratio is the minimum value $\sim1/379$ dictated by the triplet to singlet multiplicity of three and the ratio of the singlet to triplet annihilation cross sections for free positrons. The value of R shown in the figure for the Si layer is attributed to 511 keV 2γ annihilation photons Compton scattering in the detector. In our data analysis we subtract from the measured R parameters for each data set the Compton contribution obtained by subtracting the minimum value R_{min} extrapolated to infinite positron implantation energy. We estimate for Fig. 1(a) $R_{\text{min}}=0.643\pm0.007$. The fraction of the o-Ps formed in the porous film that ultimately escapes was assumed to be ~1 for the nonbarrier porous MSQ film with 0.9 keV positron implantation energy.[9]

For the 20 nm Ta barrier on Nanoglass film, the R parameter profile is shown in Fig. 1(b). When positrons are injected into the Ta barrier at 1.5 keV (equivalent depth ~5 nm), the R parameter, $R=0.648\pm0.008$, is only slightly in excess of the Compton minimum value $R_{\text{min}}=0.641\pm0.008$. This is because o-Ps cannot be formed in the nonporous Ta metal and only a few positrons are reaching the porous layer or the sample surface where Ps can be formed. As the positron energy is increased to cover the porous layer depth, a relatively large value of the R parameter, $R_{\text{peak}}=0.700\pm0.008$, is observed. The 3γ annihilation fraction is estimated as $\varepsilon=(R_{\text{peak}}-R_{\text{min}})/(R_{\text{Ps}}-R_{\text{min}})=(72\pm2)\%$

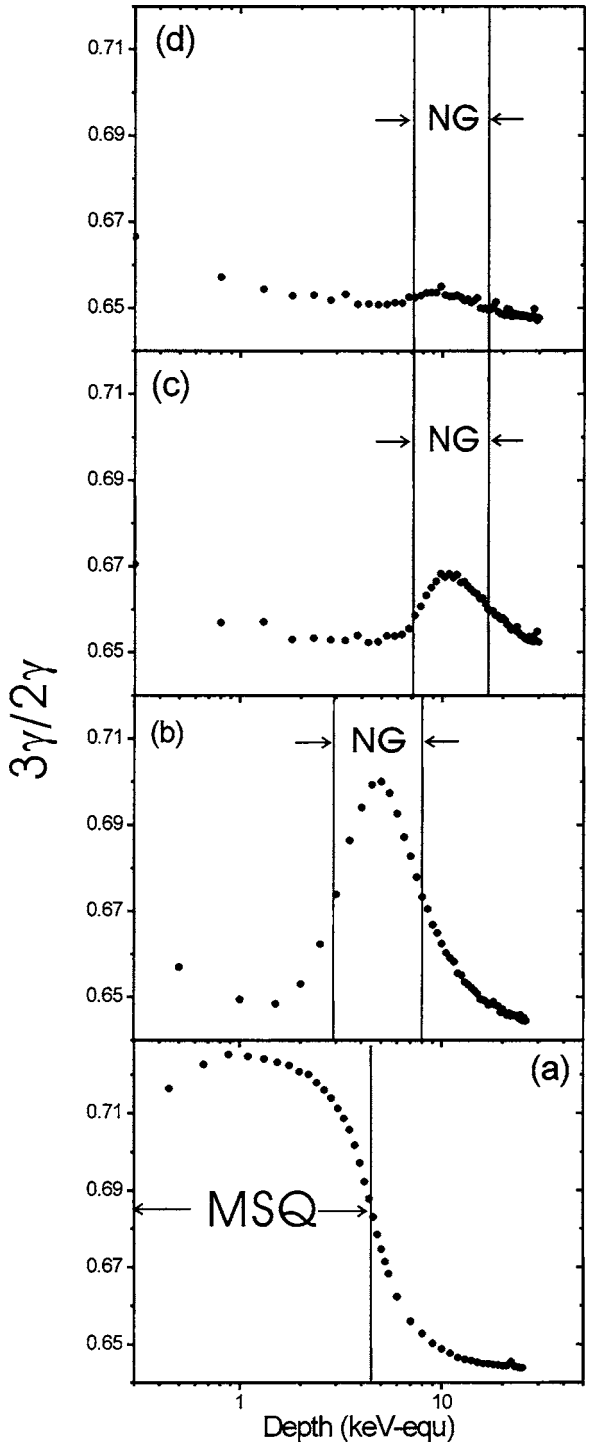

FIG. 1. Positronium three-photon annihilation parameter $R(3\gamma/2\gamma)$ as a function of positron implantation energy for four samples of porous layers deposited on Si substrates. (a) Uncapped MSQ; (b) 400 nm Nanoglass (NG), capped by 20 nm Ta; (c) same as (b) but capped by 40 nm Ta and then 100 nm Cu; (d) same as (c), but annealed at 300 °C for 1 h in Ar.

for this barrier. Apparently the barrier must have enough pinholes to allow the majority of the o-Ps to escape. In fact, pinholes have been observed in a 25-nm-thick Ta barrier via transmission electron microscopy.[10]

A porous silica Nanoglass film similar to that of Fig. 1(b) was capped first by sputtering with 40 nm Ta and then 100 nm Cu at room temperature. The R parameter is plotted in Fig. 1(c) and shows a peak $R_{\text{peak}}=0.667\pm0.008$ as the positrons are sampling the porous film. The minimum R parameter is $R_{\text{min}}=0.649\pm0.008$. Note that positron energy has shifted to 11 keV to cover the porous film depth, much higher than 5 keV used for the 20 nm Ta barrier case, but consistent with the increased thickness of the barrier. The 3γ annihilation fraction is $\varepsilon=(R_{\text{peak}}-\text{R}_{\text{min}})/(\text{R}_{\text{Ps}}-\text{R}_{\text{min}})=(22\pm1)\%$, suggesting the open area in this cap layer is much less than for the 20 nm Ta film, but clearly seen.

Annealing of Cu(100 nm)/Ta(40 nm) barriers on Nanoglass films at 100, 200, and 300 °C changes the o-Ps escaping characteristics dramatically. For 100 °C annealing, the R parameter is almost the same as that for the as-grown cap layer. Both 200 and 300 °C annealing reduces the R parameter, as shown in Fig. 1(d). When positrons were injected into the Nanoglass layer, the R parameter increased very little above the Compton background, with a peak value of $R_{\text{peak}}=0.653\pm0.009$ and $R_{\text{min}}=0.646\pm0.009$. We calculate the 3γ annihilation fraction $\varepsilon_{\text{min}}=(\text{R}_{\text{peak}}-\text{R}_{\text{min}})/(\text{R}_{\text{Ps}}-\text{R}_{\text{min}})=(9.0\pm0.3)\%$, where we assume that this small value of ε is completely due to 3γ emission from within the porous layer and is therefore the minimum value attainable in this experiment. We relate this minimum value to the annihilation rates by the equation

$$\varepsilon=\gamma_T/(\gamma_T+\gamma_P{}'), \tag{1}$$

where $\gamma_T=7.04\ \mu\text{s}^{-1}$ is the o-Ps annihilation rate in vacuum and $\gamma_P{}'$ is the effective pickoff annihilation rate of o-Ps in the porous layer, including the effects of spin-exchange collisions with the Ta barrier layer as well as collisions with paired electrons of the porous layer, the substrate and the barrier. From this equation we calculate that the effective pickoff annihilation rate in the porous film is $\gamma_P{}'=(71\pm2)\ \mu\text{s}^{-1}$.

The o-Ps density in a porous film is reduced by o-Ps 3γ annihilation, the pickoff annihilation rate, and by escaping through open holes in the surface barrier. Let the effective open area of the surface be a, the total surface area A, the thickness of the porous layer $d=400$ nm, and the o-Ps mean velocity $\bar{\nu}$. The escape rate of Ps through the surface is $\frac{1}{4}n\bar{\nu}a$ and thus the total positronium disappearance rate from the solid is $\gamma_T+\gamma_P{}'+\bar{\nu}a/4Ad$ and the total fraction of the Ps escaping is

$$F=\frac{1}{1+4Ad(\gamma_T+\gamma_P{}')/\bar{\nu}a}. \tag{2}$$

Then the relative open area, a/A, can be determined as

$$\frac{a}{A}=\frac{4d(\gamma_T+\gamma_P{}')}{\bar{\nu}}\cdot\frac{F}{1-F}. \tag{3}$$

We assume that the small R for the barrier, as shown in Fig. 1(d), is only due to 3γ annihilation inside the pores and that, after removing the Compton scattering contribution, the R parameter obtained for the nonbarrier porous MSQ film, Fig. 1(a), is all due o-Ps escaping from the porous layer. The R parameter for a set of cap layers j should be a combination of the two extremes, so that F is obtained from

$$F=(\varepsilon_j-\varepsilon_{\text{min}})/(1-\varepsilon_{\text{min}}). \tag{4}$$

For the as-grown Cu/Ta barrier, $F=0.14\pm0.01$; for the Ta 20 nm, $F=0.69\pm0.04$. The temperature of o-Ps slowing down after formation in porous MSQ would be a few times higher than room temperature after 10 or 20 ns. Assuming the average $T_{\text{Ps}}=3T$, the mean o-Ps velocity would be 9×10^6 cm/s. Putting these values into Eq. (3) we obtain

$$\frac{a}{A}=0.015\frac{F}{1-F}. \tag{5}$$

We thus calculate $a/A=(2.5\pm0.3)\times10^{-4}$ and $(3.5\pm0.3)\times10^{-2}$ for the as-grown Cu/Ta cap layer and the 20 nm Ta barrier, respectively. We note that even though the annealed Cu/Ta barrier might appear to be impermeable, it is not clear that the Ta itself is impermeable, and thus the Cu might be able to diffuse into the underlying Si.

At first glance it would seem like a typical barrier must be completely full of holes, given the large amount of positronium escaping. However, our analysis shows that the fraction of the surface that is actually being penetrated is surprisingly small. The high mean velocity of positronium in the porous material makes its escape attempt frequency large compared to the annihilation frequency, γ_p, thus allowing o-Ps to find an open area to escape even for a relatively small open area fraction. It is thus evident that Ps escape from a capped porous film is able to detect a few parts in 10^5 in the relative porosity of the capping layer. This method would be even more sensitive for detecting the open area fraction in capping layers made of passivated materials such as a-SiO_2 or organics that do not quench positronium.

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[1] Q. Yu, J. M. Bauer, J. S. Moore, and D. J. Beebe, Appl. Phys. Lett. **78**, 2589 (2001).
[2] A. Saleh and L. L. Sohn, Nano Lett. **3**, 37 (2003).
[3] R. D. Miller, Science **286**, 421 (1999).
[4] A. E. Kaloyeros and E. Eisenbraun, Annu. Rev. Mater. Sci. **30**, 363 (2000).
[5] D. W. Gidley, W. E. Frieze, T. L. Dull, J. Sun, A. F. Yee, C. V. Nguyen, and D. Y. Yoon, Appl. Phys. Lett. **76**, 1282 (2000).
[6] J. Xu, J. Moxom, S. Yang, R. Suzuki, and T. Ohdaira, Chem. Phys. Lett. **364**, 309 (2002).
[7] R. Suzuki, T. Ohdaira, Y. Shioya, and T. Ishimaru, Jpn. J. Appl. Phys., Part 2 **40**, L414 (2001).
[8] A. P. Mills, Jr. and R. J. Wilson, Phys. Rev. A **26**, 490 (1982); A. Vehanen, K. Saarinen, P. Hautojarvi, and H. Huomo, Phys. Rev. B **35**, 4606 (1987); P. G. Coleman, J. A. Baker, and N. B. Chilton, J. Phys.: Condens. Matter **5**, 8117 (1993).
[9] R. S. Yu, T. Ohdaira, R. Suzuki, K. Ito, K. Hirata, K. Sato, Y. Kobayashi, and Jun Xu, Appl. Phys. Lett. **83**, 4966 (2003).
[10] J. N. Sun, D. W. Gidley, T. L. Dull, W. E. Frieze, A. F. Yee, E. T. Ryan, S. Lin, and J. Wetzel, J. Appl. Phys. **89**, 5138 (2001).