Optica Applicata, Vol. XXXIII, No. 1, 2003

Evaluation of thin Ta(N) film integrity deposited on porous glasses

DENIS SHAMIRYAN[1,2], MIKHAIL R. BAKLANOV[3], ZOYA S. YANOVITSKAYA[4], ALEXEY V. ZVEREV[4], ZSOLT TŐKEI[1], FRANCESCA IACOPI[1,2], KAREN MAEX[1,2]

[1]IMEC, Kapeldreef 75, 3001 Leuven, Belgium, e-mail: shamir@imec.be.

[2]ESAT K.U.Leuven, Belgium.

[3]Xpeqt at IMEC, Belgium.

[4]Institute of Semiconductor Physics, 630090, Novosibirsk, Russia.

Porous glasses are widely used in microelectronics as inter-metal dielectrics with low dielectric constant (so-called low-k dielectrics). At the same time copper is used as a metal because of its low resistivity. Combination of Cu and low-k requires a barrier to prevent Cu diffusion into a low-k dielectric. Integrity of such a barrier becomes an issue when porous glass is used as a low-k dielectric. The barrier should be as thin as possible and fully dense at the same time. Using solvent (toluene) penetration through a barrier (tantalum nitride in our case, which is non-stoichiometric, hence denoted as Ta(N)) and adsorption in porous glass as a barrier integrity probe, we show that barrier integrity depends not only on porous structure of the glass, but also on its chemical composition (namely on carbon content). Glasses with high carbon content are easier to seal with Ta(N) barrier. With help of Monte Carlo simulations, we speculate that different chemical composition of the porous glass results in different surface diffusion during barrier deposition. Different surface diffusion, in turn, results in different integrity of the porous barrier.

Keywords: porous glasses, low-k dielectric, diffusion barrier, ellipsometry.

1. Introduction

Porous glasses attract much attention in microelectronic applications. As the on-chip interconnection geometry scales down, the resistance-capacitance delay becomes an important issue. The Cu interconnects instead of Al are introduced to reduce R and insulators with decreased dielectric constant k (as compared to $k = 4$ of SiO_2) are used to decrease C – so-called low-k dielectrics. The only way to obtain ultra low-k dielectrics (with $k \leq 2$) is the introduction of porosity. When part of a material is replaced by air with lowest possible $k = 1$, the total dielectric constant of the material is decreased. Due to high Cu diffusion rate, a diffusion barrier is needed between Cu

and insulator to protect porous dielectric from degradation. The integrity of such a barrier becomes an important issue, because deposition of a good quality barrier layer is difficult in the case of non-continuous substrate surface. An important task is to determine the critical barrier thickness above which it is continuous. Dependence of diffusion barrier integrity on pore size of low-k film is also to be established. In our experiments we used tantalum nitride as a barrier. The compound was non -stoichiometric (contained more Ta than N), so we use Ta(N) notation instead of TaN.

We used ellipsometric porosimetry (EP) [1] as a barrier integrity probe. In this method, adsorption of solvent (in our case toluene) in a porous film changes the film optical properties. These changes are registered by ellipsometry as different ellipsometric angles Ψ and Δ. If a fully dense barrier completely covers a porous film then no adsorption of toluene takes place. On the other hand, not fully dense barrier does not prevent toluene from adsorption in the porous film. The similar idea was used by SUNG, *et al.* [2], when positron annihilation lifetime spectroscopy with positronium as a probe was applied for barrier integrity tests.

The barrier deposition on porous glasses was simulated by a Monte Carlo model developed at Institute of Semiconductor Physics, Novosibirsk, Russia. Different chemical composition of porous glasses was simulated by applying different surface diffusion rates of tantalum nitride on different glasses.

2. Experimental

Ta(N) diffusion barrier of different thickness was deposited using ionised physical vapour deposition (IPVD) on two different porous glasses. Both glasses of 500 nm thickness were deposited on silicon substrates. The first porous glass is hydrogenselsisquioxane (HSSQ) spin-on glass (SOG) with porosity about 50%, and mean pore size close to 5 nm. Another porous glass is carbon-doped chemical vapour deposited glass (SiOCH) of 500 nm with variable porosity (10–65%) and pore size (1–10 nm) [3]. Both porous glasses are used as low-k dielectrics. Integrity of the Ta(N) barrier was investigated by means of EP. During these measurements, a sample is placed in a vacuum chamber which is slowly filled with toluene vapour until saturated pressure at room temperature is reached. Optical properties of the sample are monitored *in situ* by an ellipsometer. The barrier optical properties were also measured by conventional spectroscopic ellipsometry (SE). The SENTECH801 spectroscopic ellipsometer was used as a measurement tool.

The Ta(N) deposition was simulated using a Monte Carlo model. In the model, every event has probability to happen. The probability is described by the following equation:

$$p = A \times \exp\left(-\frac{E_a}{kT}\right)$$

where A is a pre-exponential factor, E_a is an activation energy of the event, k is the Boltzmann constant, and T is temperature. The barrier film is considered to be a set of

TaN particles. The following events were taken into account. Every particle can be adsorbed without any chance of sublimation back into the gas phase. Once adsorbed, a particle can make diffusion hops. Diffusion hops of TaN on TaN and on porous glass assumed to have different probabilities that were represented by selecting distinct activation energies.

3. Results and discussion

Adsorption of toluene inside a porous film can be clearly monitored by ellipsometric porosimetry. When no barrier is deposited, ellipsometric angles Ψ and Δ recorded during toluene pressure increase follow a theoretical curve (Fig. 1). The theoretical curve is calculated in the assumption that toluene is adsorbed inside the porous SOG changing its refractive index while the thickness is constant.

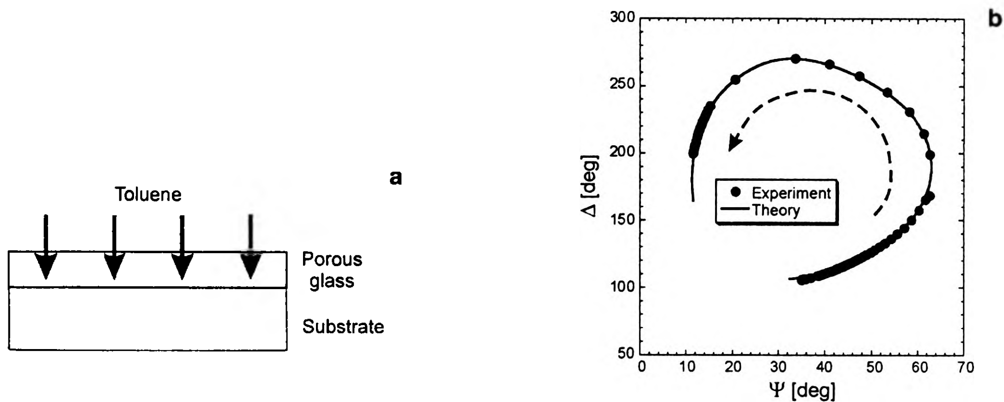


Fig. 1. Exposure of porous spin-on glass to toluene without any barrier deposited. Schematic view (**a**) and recorded Ψ/Δ diagram along with a theoretical curve, an arrow indicates pressure increase (**b**).

Deposition of 10 nm and 30 nm of Ta(N) does not prevent toluene from penetration and adsorption inside the porous SOG (the case of 30 nm Ta(N) is shown in Fig. 2). Ellipsometric angles still follow the theoretical curves. A small tile at the end of adsorption is attributed to toluene adsorption at the top surface of the barrier. Only 60 nm of Ta(N) is enough to completely seal the porous SOG (Fig. 3). In that case Ψ and Δ do not follow the theoretical curve and only a tail of surface adsorption is observed.

Using EP it is also possible to determine barrier optical properties (refractive index n and extinction coefficient k). The shape and position of the theoretical curve are strongly depending on barrier optical properties. Therefore, those properties can be determined by fitting a theoretical curve to the experimental data. Results of those fittings are presented in Fig. 4 along with n and k measured by conventional SE. Both data are in good agreement and indicate decrease of n and k for thinnest barrier. Such a decrease can be attributed to decreased density of the barrier.

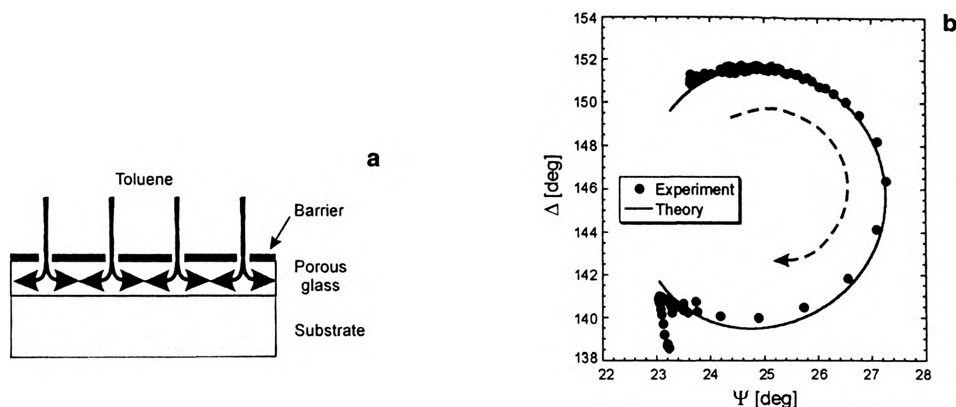


Fig. 2. Exposure of porous spin-on glass to toluene with 30 nm Ta(N) barrier on top. Schematic view (**a**) and recorded Ψ/Δ diagram along with a theoretical curve, an arrow indicates pressure increase (**b**).

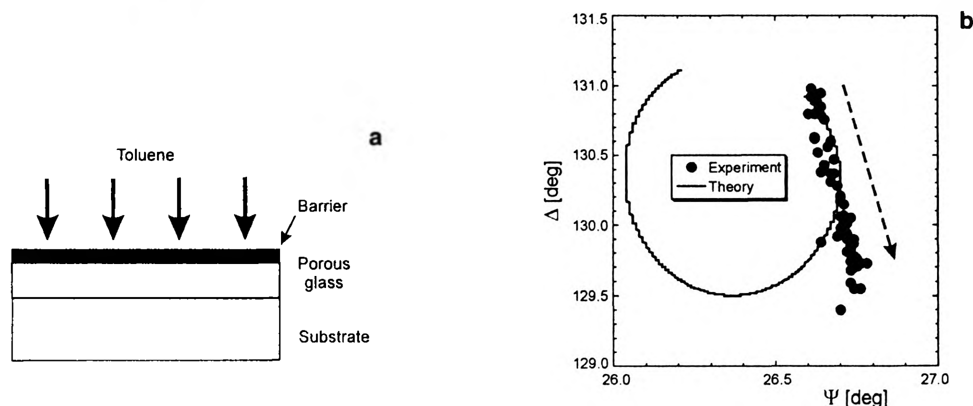
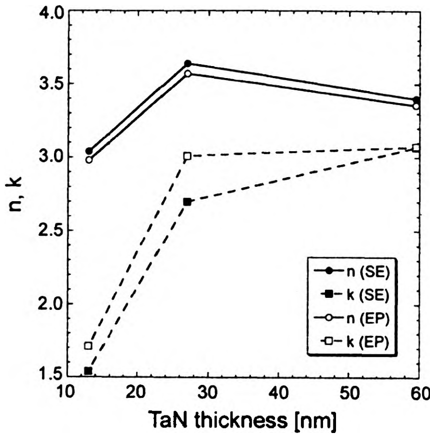


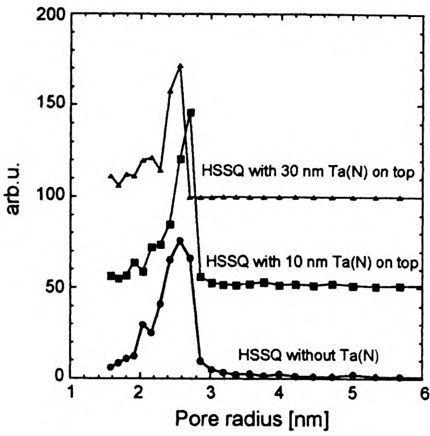
Fig. 3. Exposure of porous spin-on glass to toluene with 60 nm Ta(N) barrier on top. Schematic view (**a**) and recorded Ψ/Δ diagram along with a theoretical curve, an arrow indicates pressure increase (**b**).

Mean pore radius of porous SOG/Ta(N) system calculated from desorption isotherm (that reveals the neck size if a pore has a shape of a bottle [4]) shows minor influence of Ta(N) layer as compared to porous SOG without any barrier (Fig. 5). Only at 30 nm Ta(N) the distribution shifts a bit towards smaller sizes, indicating closure of pores by the barrier.

In the case of SiOCH film, 10 nm of Ta(N) is enough to seal the pores regardless pore size (1–10 nm) and porosity (10–60%). No change of angles Ψ and Δ has been observed at any pressure implying complete sealing of the porous film by the barrier. Since porous structure of porous SOG and SiOCH is similar one can assume the chemical composition to play an important role in the sealing process.

Aforementioned difference between two porous films could be explained by different surface diffusion of Ta(N) during deposition. If surface diffusion is high (porous HSSQ) then deposited barrier can penetrate the porous film by pore walls





▲

Fig. 4. Refractive index *n* and extinction coefficient *k* of Ta(N) deposited on porous SOG. Measurements were done by spectroscopic ellipsometry and ellipsometric porosimetry.

Fig. 5. Pore radius distributions for SOG without a barrier (circles), with a 10 nm TaN barrier (squares), and with a 30 nm TaN barrier (triangles). The latter has smaller pores in the barrier.

without forming a sealing layer on the top surface. On the other hand, if surface diffusion is low (SiOCH) then Ta(N) forms a continuous layer on the top surface without penetrating deep into the porous film.

Assumption of different surface diffusion is supported by simulation results. Figure 6 shows pore cross-sections after simulation of Ta(N) deposition on two porous films. The only difference between the films is the activation energy of Ta(N)/film surface diffusion ($E_{TaN/film}$). Although the determination of absolute values of the activation energies of surface diffusion is rather complicated, activation energy ratio between TaN self-diffusion and TaN/film diffusion can be used for process description.

Decreased surface diffusion of Ta(N) during deposition and, therefore, continuous barrier formation can be caused by the presence of carbon in the glass. A glass containing no carbon (HSSQ) can be sealed by about 50 nm Ta(N), whereas 20% of carbon in SiOCH allows 10 nm Ta(N) to seal a porous glass. We also found the same trend for sealing of porous glasses with different carbon content: higher C

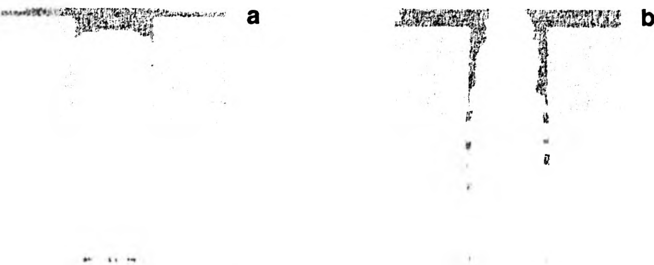


Fig. 6. Simulated cross-section of Ta(N) on porous substrate: **a** – SiOCH: low surface diffusion ($E_{TaN/SiOCH}/E_{TaN/TaN} = 1.1$), **b** – SOG: high surface diffusion ($E_{TaN/SOG}/E_{TaN/TaN} = 1.7$).

concentration leads to faster sealing of the pores [5]. Ta is known to easily form Ta–C bonds due to high formation enthalpy ($\Delta_f H^0$(TaC) = –34.44 kcal/mol) [6] and TaC was found on Ta/C (or TaN/C) containing film interface [7]. Therefore, Ta(N) diffusion on the film surface is slowed down by interaction with carbon (if present).

4. Conclusions

We showed that ellipsometric porosimetry could be used for characterization of the diffusion barrier integrity deposited on porous glasses. Using EP we found that the integrity of the IPVD Ta(N) diffusion barrier depends not only on pore size of porous glass, but also on its chemical nature (carbon content in our case). Increased carbon content results in easier sealing of the porous glass by a Ta(N) barrier. Basing on Monte Carlo simulation, we assume that carbon reduces surface diffusion during barrier deposition and allows the barrier to form a continuous layer on the top surface of the porous glass. Absence of carbon results in porous 30 nm Ta(N) barrier on porous SOG whereas 10 nm Ta(N) is non-porous on porous SiOCH (which has about 20% of carbon in composition).

References

[1] DULTSEV F.N., BAKLANOV M.R., Electrochem. Solid State Lett. **2** (1999), 192.

[2] SUNG J.-N., GIDLEY D.W., DULL T.L., FRIEZE W.E., YEE A.F., RYAN E.T., LIN S., WETZEL J., J. Appl. Phys. **89** (2001), 5138.

[3] SHAMIRYAN D., BAKLANOV M.R., VANHAELEMEERSCH S., MAEX K., Electrochem. Solid State Lett. **4** (2001), F3.

[4] GREGG S.J., SING K.S.W., *Adsorption, Surface Area and Porosity,* 2nd edition, Academic Press, London, New York 1982, p. 195.

[5] IACOPI F.,TŐKEI ZS., LE Q.T., SHAMIRYAN D.,CONARD T., BRIJS B., KREISSIG U., VAN HOVE M., MAEX K., J. Appl. Phys. **92** (2002), 1548.

[6] GERSTENBERG K.W., GRISCHKE M., J. Appl. Phys. **69** (1991), 736.

[7] YANG G.R., ZHAO Y.P., WANG B., BARNAT E., MCDONALD J., LU T.M., Appl. Phys. Lett. **72** (1998), 1846.

Received September 26, 2002