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Citation: *Appl. Phys. Lett.* **98**, 121902 (2011); doi: 10.1063/1.3567537

View online: <http://dx.doi.org/10.1063/1.3567537>

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Mechanical properties of ultralow-dielectric-constant mesoporous amorphous silica structures: Effects of pore morphology and loading mode

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(Received 1 December 2010; accepted 25 February 2011; published online 21 March 2011)

We report results for the dependence of the mechanical properties of ordered mesoporous silica structures on the pore diameter based on molecular-dynamics simulations. We examine structures with spherical pores arranged in a simple cubic lattice and cylindrical pores arranged in a square lattice subjected to uniaxial tension and compression; for the structures with cylindrical pores, both radial and axial loading is studied with respect to the pore orientation. Our analysis provides a unifying explanation to the observed mechanical response based on the mechanical loading effects on the pore wall thickness. © 2011 American Institute of Physics. [doi:10.1063/1.3567537]

The continuously increasing integration scales in high-performance microelectronic devices lead to increasingly closer spacing between interconnect lines and require an ultralow dielectric constant (ultralow- k) of the dielectric material to reduce the capacitive coupling and avoid the cross-talk between the interconnects.¹ Lowering the dielectric constant of silica, the traditional dielectric material in microelectronic technologies, is accomplished by decreasing the material's density; such density reduction can be detrimental to the mechanical strength of the device back-end structures, which have to tolerate high levels of thermomechanical stress that are characteristic of semiconductor manufacturing processes, chip packaging, and device service.¹ Porous amorphous silicates, compatible with current device fabrication technologies, are particularly promising ultralow- k dielectric materials;²⁻⁵ however, the deterioration of their mechanical properties upon density reduction has been established.⁶

Atomic-scale computational studies based on molecular-dynamics (MD) simulations have been used to investigate structural properties and the mechanical behavior of amorphous silica structures.⁷⁻¹⁰ The mechanical properties of ordered mesoporous silica structures also have been studied by such atomistic simulations either indirectly, aiming at understanding the role of the pore wall thickness,⁶ or directly by studying the dependence of the elastic modulus on the mesoporous silica density and on the mesopore size.¹¹ In a recent study, we found based on MD simulations that in ordered mesoporous silica structures consisting of regular arrays of spherical pores an elastic instability can be triggered under uniaxial compressive straining for densities or pore diameters lower than certain critical values.¹¹

The purpose of this letter is to determine the mechanical properties of ordered mesoporous silica structures as a function of the pore diameter and examine systematically the effects on these mechanical properties of different pore morphologies and straining modes. By examining structures with spherical pores arranged in simple cubic lattices under both

uniaxial tension and compression, as well as structures with cylindrical pores arranged in square lattices under both uniaxial tension and compression with the loading direction both parallel and perpendicular to the cylindrical pore axes, we provide a unifying explanation for the observed mechanical response based on the beneficial or detrimental effects of the mechanical loading on the pore wall thickness.

Our computational study is based on MD simulations, as described in Ref. 11, according to a realistic many-body interatomic potential for silica.^{12,13} We generated the normal-density amorphous SiO₂ (a-SiO₂) phase by a thermal vitrification process;¹¹ this consisted of isochoric melting of a β -cristobalite crystal and subsequent quenching of the melt, followed by annealing of the resulting vitrified state at room temperature and volume relaxation of this amorphous phase. By removing material from this normal-density a-SiO₂ phase, we generated ordered mesoporous structures of given density, pore morphology, pore size, and pore arrangement, which were then annealed at room temperature for structural relaxation. After these preparation stages, we analyzed the mechanical behavior of the ordered mesoporous a-SiO₂ structures based on MD simulation of dynamic straining (at constant strain rate and temperature) followed by isothermal-isostress MD simulation. As part of the mechanical behavior analysis, we calculated the elastic moduli, M , of the ordered mesoporous structures according to the relation $\Delta E = M\varepsilon^2/2$, where ΔE is the elastically stored potential energy during the uniaxial straining stage for dynamic straining of the mesoporous material up to strain level ε .¹¹ The above $\Delta E(\varepsilon)$ relation, on which the M computation is based, is valid for linear elastic response of the strained structures; our MD simulations of dynamic straining have confirmed that the mechanical response is indeed linearly elastic for the stable mesoporous structures that we investigated for a maximum strain level of 2%. This computational model yielded a sublinear power-law dependence of the Young modulus on density for ordered mesoporous silica structures with spherical pores arranged in a simple cubic lattice,¹¹ in agreement with recent experimental data.⁶

In this study, we have examined systematically the response of ordered amorphous mesoporous silica structures

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FIG. 1. (Color online) Dependence of the elastic modulus, M/M_0 , on the pore diameter, d , for ordered mesoporous silica structures with spherical pores arranged in a simple cubic lattice and density $\rho=0.88 \rho_0$. Results are shown for both tensile and compressive uniaxial straining up to a strain level of 2%.

with spherical pores arranged in a simple cubic lattice to tensile uniaxial straining and of ordered mesoporous structures with cylindrical pores arranged in a square lattice to both tensile and compressive uniaxial straining. The response of the former category of ordered mesoporous silicas to compressive straining was reported in Ref. 11. The MD simulations were performed as described in Ref. 11 by applying periodic boundary conditions in the two principal directions normal to the applied strain, while keeping the corresponding supercell dimensions fixed. This simulation setup provides a good representation of the mechanical state of thin films used as interlayer dielectrics in microelectronic devices. Figure 1 shows the dependence of the elastic modulus M on the pore diameter d for ordered mesoporous structures with spherical pores; the density is $\rho=0.88 \rho_0$, where ρ_0 is the normal density of the amorphous phase, and M is reported in terms of M/M_0 , i.e., with respect to the modulus M_0 of the normal-density amorphous phase.¹¹ Results are shown for both tensile and compressive straining up to a strain level of 2%. In both cases, M/M_0 is seen to decrease monotonically with decreasing d ; however, the elastic modulus is consistently higher in the tensile straining case. Moreover, in the tensile straining case, loss of structural stability triggered by a vanishing elastic modulus is not observed, i.e., $M/M_0 > 0$ consistently for tensile straining; on the contrary, at low d ($d = 1.25$ nm), M is negative under compressive straining.¹¹ The most important conclusion that can be drawn from these comparisons is that the applied tensile strain has a beneficial effect on the pore wall thickness, h_w , that is responsible for the mechanical stabilization of mesoporous structures with smaller-size pores: we attribute the observed stabilizing effect at low d to the increase in h_w due to the applied tension.

Our results for the mechanical properties of ordered mesoporous silica structures with cylindrical pores arranged in a square lattice are reported in Fig. 2. Figure 2(a) shows the dependence of the elastic modulus M on the cylindrical pore diameter d under uniaxial compressive straining up to a strain level of 2% for a density $\rho=0.88 \rho_0$. For these cylindrical pore arrangements, two cases were analyzed where the compressive load was oriented parallel and perpendicularly to the cylindrical pore axes, i.e., cases of “axial” and “radial” straining with respect to the cylindrical pore orientation. In both of these cases, M decreases with decreasing d ; this is consistent with the case of spherical pores arranged in a

FIG. 2. (Color online) Dependence of the elastic modulus, M/M_0 , on the pore diameter, d , for ordered mesoporous silica structures with cylindrical pores arranged in a square lattice and density $\rho=0.88 \rho_0$ under (a) uniaxial compressive and (b) uniaxial tensile straining up to a strain level of 2%. In both cases, the calculated modulus as a function of d for structures with the same density and spherical pores arranged in a simple cubic lattice is shown for reference. For the structures with cylindrical pore morphology, the insets in (a) and (b) give schematic representations of the loading modes examined.

simple cubic lattice, Fig. 1. We find that these ordered mesoporous structures are stronger under axial compressive loading, i.e., when the compressive load is aligned with the direction of the cylindrical pore axes. This mechanical response can be understood on the basis of the loading mode effects on the cylindrical pore wall thickness, h_w . Specifically, applying compression normal and parallel to the cylindrical pore axes [as shown in the insets in Fig. 2(a)] leads to a decrease and increase, respectively, in h_w ; thicker pore walls result in increased mechanical strength.

The mechanical properties of ordered mesoporous structures with cylindrical pores in a square lattice under tension are reported in Fig. 2(b) and compared with those of ordered mesoporous structures with spherical pores arranged in a simple cubic lattice; in all cases, the results are from MD simulations of uniaxial tensile straining up to a strain level of 2% for a density $\rho=0.88 \rho_0$. In the case of cylindrical pores, we examine both axial and radial tension in terms of the orientation of the load with respect to the cylindrical pore axes [as shown in the insets in Fig. 2(b)]. Consistently with Figs. 1 and 2(a), the dependence of the elastic modulus M on the pore diameter d is reported. In all cases, M decreases with decreasing d . However, the mesoporous structures with cylindrical pores are seen to be weaker than those with spherical pores. We attribute this effect to the larger pore surface area of the cylindrical pores and the thinning of the pore walls over such larger area. Furthermore, we observe that mesoporous structures with cylindrical pores are slightly stronger under radial tension than under axial tension; this is in contrast to their mechanical response in the case of uniaxial compression. We interpret this response based on the beneficial effect of the radial tension on the pore wall thickness, h_w : radial tension leads to an increase in h_w , while axial tension causes a decrease in h_w .

Using the results of Fig. 2, we can also carry out a comparison of the mechanical properties of the mesoporous structures with cylindrical pores under tensile and compressive loads. This is done in Figs. 3(a) and 3(b) by comparing the corresponding M versus d dependences; the insets in these figures show the two different loading modes under which the elastic moduli, M , are compared. Figure 3 shows that for both axial and radial loading, the structures are stronger under tension than under compression and that all the

FIG. 3. (Color online) Comparison of the mechanical properties under tension and compression of the mesoporous structures with cylindrical pores arranged in a square lattice for straining in the (a) axial and (b) radial direction based on the results of Fig. 2.

mesoporous structures are stable under tension, even those with very small pore diameters (e.g., $d=1.25$ nm). We attribute this mechanical stabilization of the structures with the smaller pores to the beneficial effect on the pore wall thickness h_w caused by the tensile strain. In addition, comparing the results of Figs. 3(a) and 3(b) shows greater differences in the elastic moduli under radial loading than under axial loading. This is due to the alignment of the mechanical load with the direction of pore growth under radial loading, which has a direct effect on h_w ; this effect is beneficial in the case of tensile loading and detrimental in the case of compressive loading.

Finally, we mention that we have also examined effects of heat treatment of the mesoporous structures on their mechanical properties. Specifically, we annealed ordered mesoporous structures with spherical pores arranged in a simple cubic lattice and $\rho=0.88 \rho_0$ for time periods that were sufficient for thermal equilibration. We heat treated structures with pore diameters $d=5$ and 1.25 nm at temperatures $T=500$, 700 , and 1000 K and then cooled them down gradually (over 10 – 15 ps) to 300 K. We found that thermal annealing of the structures with $d=1.25$ nm at all the temperatures examined leads to loss of their structural stability. For the stable structures with $d=5$ nm, we calculated their elastic moduli during uniaxial compressive straining. We found that heat treatment improves the elastic modulus but the effect is not significant: M increases with T up to an additional 4% of M_0 for the highest annealing temperature examined.

In conclusion, our results paint a comprehensive picture for the mechanical response to uniaxial straining of ordered mesoporous a-SiO₂ structures, which can be understood on the basis of the effects that the applied loading has on the pore wall thickness, h_w . For spherical pores arranged in a simple cubic lattice, $h_w=d \{[(6/\pi)(1-\rho/\rho_0)]^{-1/3}-1\}$. For cylindrical pores arranged in a square lattice, $h_w=d \{[(4/\pi)(1-\rho/\rho_0)]^{-1/2}-1\}$. In both cases, $h_w \propto d$, which explains the decrease in M with decreasing d , through the corresponding decrease in h_w . In the case of spherical pores in a simple cubic lattice arrangement (at given d and ρ), applied tension and compression cause an overall increase and decrease, respectively, in h_w in the direction of the applied uniaxial loading. Consequently, the structures are stronger under tension. For cylindrical pores in a square lattice arrangement (at given d and ρ), applied axial and radial compression cause an overall increase and decrease, respectively, in h_w , resulting in stronger structures under axial compression. For the same pore morphology and arrangement, however, applied

axial and radial tension cause an overall decrease and increase, respectively, in h_w , leading to stronger structures under radial tension. The above descriptions of the changes in h_w under uniaxial tension or compression that we have used to explain our results for the modulus dependence on pore diameter are based on the mechanics of a linearly elastic medium. For completeness, these changes also are consistent with direct measurements of the wall thickness after the MD simulations of dynamic deformation.

For liquid silica slabs, it has been shown that ion coordination, ring size, local density, and local elastic modulus differ near surfaces as compared to their bulk values.¹⁴ Structural relaxation near pore surfaces and curvature effects as the pore size decreases also result in structural changes near the pore surfaces in the mesoporous structures that we have investigated. Correlating structural changes from the inner wall regions to the pore surfaces with the resulting mechanical properties is beyond the scope of the present study. However, the key qualitative trend that the elastic modulus of the mesoporous materials decreases with decreasing pore diameter, and, therefore, with decreasing pore wall thickness, has been consistent over the entire range of parameters that we have examined.

The results of our atomic-scale analysis provide experimentally testable hypotheses for the synthesis of ordered mesoporous silica structures with improved mechanical properties. Quantitative predictions of elastic moduli at given temperature as functions of density, pore size, and applied strain, $M(\rho, d, \epsilon)$, for various pore morphologies and arrangements and determination of the corresponding elastic stability domain boundaries, i.e., regions in parameter space where $M(\rho, d, \epsilon) \rightarrow 0$, require further fundamental theoretical studies of the mechanical behavior of mesoporous amorphous structures.

This work was supported by the National Science Foundation through Grant Nos. CBET-0304159, CBET-0417770, and CMMI-0531171.

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