Bromley et al. Reply: In our Letter [1] we explicitly demonstrate that defect-terminated SiO_2 chain clusters may be stabilized as fully coordinated rings, and speculate that "...we envisage... fully connected clusters, such as our molecular rings, as materials building blocks." In their Comment [2], Sun et al. propose SiO_2 clusters possessing terminating defects but lower energies as building blocks. While never claiming that SiO_2 rings have particularly low energies, we hold that the suitability of a cluster/molecule to act as a material building block is not primarily determined by its energy, but by other criteria: (i) structural stability, (ii) thermodynamic accessibility, (iii) formation selectivity, and (iv) resistance to coalescence. We stress that there is no requirement for a cluster's structural stability to be dependent on its energy. $Si_{12}O_{24}$ rings, as tested by molecular dynamics ($T \sim 1000$ K), for example, are particularly resistant to collapse or rupture. The energy of a cluster/molecule is also often a poor guide to the ease with which it may be formed. In recent plasma experiments, for example, ground state clusters are not necessarily, or even usually, formed, but, rather, metastable clusters [3]. For thermodynamic accessibility, (ii), it is thus not sufficient that a potential building block has relatively low energy. For our $(SiO_2)_N$ rings, formation could be envisaged by deformations of long two-ring chains, or linking smaller chains, both thermodynamically downhill processes [1]. As it has long been established that two-ring chains of arbitrary length can be synthesized in the formation of silica-W [4], and that two-ring chain clusters are formed in (Si,O)-plasma reactions [5], the manipulation of such sources indicates viable routes to ring formation. We note that the proposed low energy SiO_2 building blocks of Sun et al. are also not ground state clusters [see Figs. 1(a) and 1(b)], nor is any route to their formation obvious to us. Building blocks can be utilized only if made in large quantities, thus, ideally, one would like them to be selectively identifiable. Our rings have IR bands at 886, 902, and 933 cm^{-1}. Jena et al. pointed out that their $Si_{12}O_{24}$ cluster also has similar bands, seemingly making identification difficult [2]. We note, however, that their structure also has numerous other significant bands (e.g., $\sim$827, $\sim$951 cm^{-1}), which are not present in the spectra of the rings [6]. Furthermore, both the rings and the fully coordinated cage [see Fig. 1(b)] have particularly high ionization potentials facilitating their separation as neutral species from an ionizing environment. Finally, criterion (iv) provides, we feel, the defining property of a cluster-based, or molecular material, i.e., being an assembly of interacting but *discrete* structurally stable units. High relative reactive stability is thus of great importance when bringing clusters together to form a material. Terminated SiO_2 clusters are particularly reactive to each other and are thus prone to coalesce [2], losing their discrete structural integrity. Coalescence is inherently avoided with fully coordinated clusters, which also often display correspondingly large
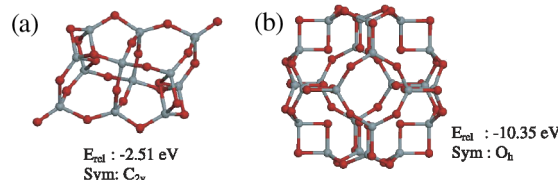

FIG. 1 (color online). (a) A $Si_{12}O_{24}$ cluster 2.51 eV lower in energy [O:6-311 + G(d, p), Si:6-31G*/B3LYP, GAUSSIAN 98 [7]] than the low energy $Si_{12}O_{24}$ cluster by Sun et al. (b) A fully coordinated $Si_{24}O_{48}$ cage 10.35 eV lower in energy and with a HOMO-LUMO gap 0.78 eV ($IP_v = 9.39$ eV) larger than the terminated $Si_{24}O_{48}$ cluster by Sun et al. (6-31G*/B3LYP).

ε_{LUMO}-ε_{HOMO} gaps. Furthermore, although the curvature and bonding strain of fully coordinated clusters can play an adverse energetic role, with increasing $(SiO_2)_N$ cluster size this effect becomes progressively smaller. We show in Fig. 1(b) that such stabilization is not only observed in our SiO_2 rings, with a fully coordinated $Si_{24}O_{48}$ cage-like cluster over 10 eV lower in energy than the terminated $Si_{24}O_{48}$ cluster proposed by Sun et al.

Many materials formed by the assembly of metastable discrete units are known (e.g., C_{60} derivatives, conducting organics, molecular magnets), often with ring-like building units. Based on the properties of the chain-based silica-W [4], we speculate that a SiO_2 ring-based material would be ordered, have a low refractive index (RI $\sim$ 1.41), density ($\rho \sim 1.97$ g/cm^3), and dielectric constant (k). The weak ring-ring interactions and their disklike form also raise the possibility of liquid crystalline behavior with transitions between various (dis)ordered states with respective changes in RI, ρ, and k.

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