interfacial dielectric constant will probably be between that of Si and SiO₂. The altered dielectric layers are not accounted for in our ellipsometric measurements, in which we assume that the oxide has only the dielectric constant of bulk SiO₂. This is probably why ellipsometry has underestimated the width of the oxides in Fig. 3. The probe localization is obtained by constructing a wavepacket with a transverse momentum spread of more than a reciprocal lattice vector, and consequently all electronic momentum information is lost (as required by the uncertainty principle). Therefore these evanescent states responsible for tunnelling through the oxide and the states from the extended conduction band are treated on an equal footing, and cannot be separated in such a local measurement. In the simplest model, the silicon wavefunctions decay exponentially into the oxide with a decay length for the evanescent states, \( \lambda(E) \), determined by the energy difference between the interfacial state (\( E \)) and the conduction band edge of bulk SiO₂ (\( E_o \)), as \( \lambda(E) = h/(E_o - E) \). The tunnelling current depends on the overlap of the evanescent states from either interface. A satisfactory tunnelling barrier is formed when the oxide thickness \( t \) is \( 6\lambda \). This sets an absolute minimum thickness of \( t_{min} = 0.7 \, \text{nm} \) for an ideal SiO₂ gate oxide. Interfacial roughness adds another \( \delta r \) to \( t_{min} \). The smallest roughness for our thermally grown oxides was \( \delta r = 0.6 \, \text{nm} \) which puts a lower limit of 1.2 nm on the practical SiO₂ gate oxide thickness. The induced gap states also place severe constraints on the minimum allowed thickness for alternative dielectrics, many of which have large dielectric constants, but reduced bandgaps and hence longer decay lengths. Furthermore, there is the possibility of a reaction between the dielectric and the silicon substrate to form a silicon oxide interlayer. If the interlayer thickness exceeds 1.3 nm (and a typical native oxide is 2 nm thick), the gate capacitance is less than what could be obtained with a pure SiO₂ gate oxide.

Received 20 January; accepted 8 April 1999.


Acknowledgements. We thank D. R. Hammond, M. S. Hybertsen, P. Rez, J. Neuton and B. Ratlogg for discussions, and J. Silcox and M. Thomas for access to the Cornell Center for Materials Research STEM. Funding for the operation and acquisition of the STEM was provided by the NSF. Upgrades were founded by the NSF. We thank D. R. Hammann, M. S. Hybertsen, P. Rez, J. Neuton and B. Ratlogg for discussions, and J. Silcox and M. Thomas for access to the Cornell Center for Materials Research STEM. Funding for the operation and acquisition of the STEM was provided by the NSF. Upgrades were founded.
molecule was stretched, the force–extension curve revealed a sawtooth pattern. Using titin constructs, Rief et al.\(^\text{19}\) demonstrated that every peak in the sawtooth pattern corresponded to a single domain unfolding. Apparently, it is the cumulative effect of the intermediate-strength hydrophobic bonds in the immunoglobulin-like domains of titin which contribute to the sawtooth force–distance curves found for this molecule\(^{20,21}\). Studies using optical tweezers corroborated these results\(^{22–24}\). These initial studies demonstrate that individual titin subunits unfold one at a time, suggesting that this technique affords an opportunity to delineate some of nature’s mechanisms in building modular elastic fibres.

We have used this technique to investigate the molecules that hold abalone shells together. Figure 2 shows force–extension curves for the organic material exposed on a freshly cleaved nacre surface. Breaking forces of the order of 100–400 pN are seen in these curves. The hysteresis observed after a complete pulling cycle demonstrates that bonds of some kind are breaking and reforming. As lustrin A is present on that surface, it is possible that we observed unfolding of this protein. However, and this is the key point, the mechanism behind the strength and toughness of the adhesive is revealed by the force–extension curves and does not depend on the identification of the specific molecules involved. This behaviour may reflect the successive opening of intra-chain loops or folded domains within a single molecule, or the successive release of sacrificial inter-chain bonds holding a crosslinked multichain matrix together.

To demonstrate the effect that a material with this type of force–extension curve can have on the properties of an adhesive made from modular fibres, we consider three different cases. Gluing materials together with conventional adhesives has traditionally involved either relatively stiff adhesives such as epoxies, or elastic adhesives such as silicon adhesives. When pulling on two surfaces glued together with a short molecule, the pulling force increases rapidly with only a little extension of the molecule (Fig. 3). First, a perfect stiff adhesive would be a short molecule bound to each surface by strong (that is, covalent or ionic) bonds and the molecules of the adhesive itself would be held together with strong bonds. Thus the break strength of each adhesive molecule would be the force required to break a strong bond: of the order of one nanonewton (estimated by dividing one electron volt by an extension of one Ångström). For a material with many strongly bound molecules in parallel, the macroscopic tensile strength is expected to be of the order of several gigapascals. This is the order of magnitude for the breaking force of strong polymers such as Kevlar\(^{25,26}\). The fracture toughness of such materials is rather small, however, even though the forces are large. This can be understood by considering the area under the force–extension curve (Fig. 3), which is the energy required to break the material.

Second, in contrast to this behaviour, the idealized curve for an elastic fibre made of long molecules shows that the force increases.

---

**Figure 1** Scanning and transmission electron micrographs of a freshly cleaved abalone shell, showing adhesive ligaments formed between nacre tablets. **a**, Scanning electron micrograph of a freshly cleaved abalone shell showing adhesive ligaments formed between consecutive abalone nacre tablets on exertion of mechanical stress. The tablets are ~400 nm thick. **b**, Transmission electron micrograph of another cleaved abalone shell, showing the adhesive ligaments between nacre tablets. The space between the tablets is ~600 nm. Thus the ligaments can lengthen to many times the original spacing between the tablets, which is of the order of 30 nm.

**Figure 2** Consecutive force–extension curves, obtained using an atomic force microscope, from pulling on a freshly cleaved abalone nacre surface. Rupture events, with a sawtooth appearance, are visible in each of the curves. The surface was not touched between pulls, strong evidence that some refolding took place, possibly of domains in lustrin A. The approach and retract curves show hysteresis, indicating that the rupture events dissipate energy.
slowly as the elastic material is stretched to the point at which the elastic limit is reached (Fig. 3)\textsuperscript{27,28}. Then the force increases rapidly as the elastic material is stretched to the point at which the polymers break at forces of the order of 1 nN, modules unfold at intermediate forces (0.1–0.7 nN). Repeated unfolding of molecules allows stretching up to large extensions, required significant energy. Therefore, a long molecule that is compacted into domains that are held together with intermediate-strength bonds combines both high (tensile) strength and high toughness.

Figure 3

![Force-extension curves for three different kinds of polymers.](image)

**Figure 3** Model of long polymers and force-extension curves for different kinds of polymers. a. Diagram of long polymers behaving as entropic springs. The lower molecule is compacted, with many domains that are held together with intermediate-strength sacrificial bonds. b. Force-extension curves for three different kinds of polymers. A short molecule (solid curve) resists pulling up to a high force before it breaks at small extensions. The energy required to break this short molecule (area under the curve) is small. A long molecule (hatched curve) behaves like an entropic spring and yields to the pulling force up to large extensions. The energy to break the long molecule is larger than that for the small molecule, but the forces at low extensions are small. But a long molecule that is compacted into domains (the stippled plus the hatched curve) that are held together with intermediate-strength bonds resists pulling already at small extensions. Before the molecule’s backbone can break at forces of the order of 1 nN, modules unfold at intermediate forces (0.1–0.7 nN). Repeated unfolding of molecules allows stretching up to large extensions, required significant energy. Therefore, a long molecule that is compacted into domains that are held together with intermediate-strength bonds combines both high (tensile) strength and high toughness.

Third, an adhesive or fibre that combines both high strength and high toughness. Real elastic materials such as rubbers have tensile strengths that are lower than the force of a nanonewton or so that breaks strong bonds in natural materials, proteins provide the modular fibre: but this mechanism should work for other polymers, as long as it is possible to compact the length of the polymers using intermediate-strength bonds that break sacrificially with forces comparable to, but less than, the force of a nanonewton so that breaks strong bonds in the polymer backbone.

Received 26 February; accepted 20 April 1999.