Molecular Confinement in Nanometer-Size Superlattice Microstructures

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Using lithographic techniques, we have prepared two-dimensional pores with widths controllable in the range 10–100 Å. These materials are formed from amorphous superlattices consisting of alternating layers of silicon and silicon dioxide by use of a selective etch. The micropores adsorb hydrocarbons from solution in a size-selective manner. The effects of confinement in these molecular-scale structures are observed by fluorescence spectroscopy: We demonstrate that pyrene molecules trapped in 20-Å pores lack the mobility necessary to form dimers.

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Since the invention of the integrated circuit, lithographic techniques have been used to prepare smaller and smaller devices with carefully controlled dimensions. Microstructures have been extensively used to investigate electronic effects[1] and mechanical devices.[2] However, the observation of chemical effects in microstructures requires smaller dimensions and greater surface area than has been possible to date. In this Letter we report molecular confinement in the smallest of all lithographically fabricated microstructures. These microstructures have monodisperse pores which can be fabricated in sizes as small as those present in zeolites[3] (≤ 10 Å). For this reason they are ideal model systems for the study of molecular dynamics in confined spaces, such as those commonly used in chemical separations.

We have prepared molecular-size pores utilizing the arrangement of ultrathin layers in superlattice materials.[4] The layer edges are exposed with lithographic patterning and two-dimensional slots are formed by selective etching of one of the two layers making up the superlattice. Aromatic molecules can be adsorbed into the structure if they are smaller than the pore width, which is controlled by the layer thickness. The fluorescence spectra of these molecules show the effects of confinement in such small structures. Specifically, we demonstrate that the fluorescence of trapped pyrene depends upon the pore size, with small pores exhibiting decreased dimer formation probability. This is a result of the lower mobility in molecular-size spaces.

Superlattice micropores were prepared from amorphous superlattices[5] consisting of layers of hydrogenated amorphous silicon (*a*-Si:H) alternating with amorphous silicon oxide (*a*-SiO_x:H). The interfaces in similar amorphous silicon superlattices have previously been shown to be nearly atomically abrupt both structurally[6] and electronically.[7] This abruptness is essential in order to control the micropore dimensions to the atomic scale. To expose the layer edges over a large area, we use natural lithography.[8] In this technique a monolayer of polystyrene spheres 0.2 μm in diameter is put down onto the superlattice as an etchant mask [Fig. 1(a)]. Reactive ion milling is used to remove the material between the spheres, leaving a textured surface like that in Fig. 1(b). The sample is then exposed to a chemically selective etch to partially remove one of the layers and to form the micropores [Fig. 1(c)]. For example, the microstructure shown in Fig. 2 was prepared from an amorphous silicon–silicon oxide superlattice by use of gaseous XeF_2 to etch away the silicon layers.[9] The pores in this sample are 30 Å wide and 500 Å deep. The pore width is within 5 Å of the original silicon layer thickness, showing the chemical abruptness of the interfaces. Typical samples have $> 10^{10}$ such pores over 1 cm^2. The width and composition of the pores can be controlled by variation of the deposition times and materials. We have prepared slot widths from ~ 8 Å to greater than 100 Å in this manner. The dependence of the width of the layers on deposition time was determined from measurements of the bulk index of refraction[10] and the reflectivity determined *in situ* during the deposition.[11]

Before the adsorption of molecules into these struc-

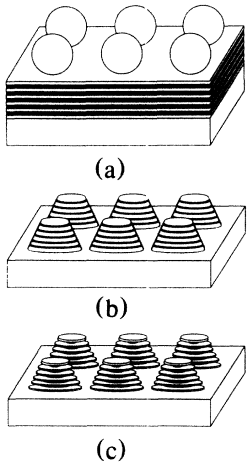

FIG. 1. Schematic illustration of the lithographic process for making superlattice micropores (a) before milling, (b) after argon milling, and (c) after selective etch to remove one layer type.

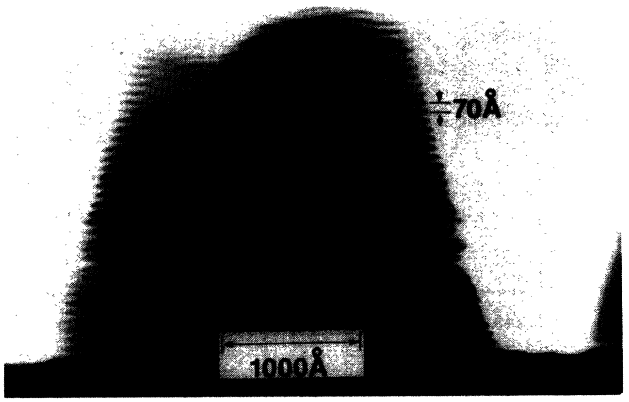

FIG. 2. Transmission electron micrograph of a-Si:H/a-SiO_x:H superlattice which has been etched in XeF_2 to remove the silicon layers. The repeat distance is 70 Å, with slot widths of 30 Å. The contrast in the slotted region is amplitude dominated and present only after the selective etching process.

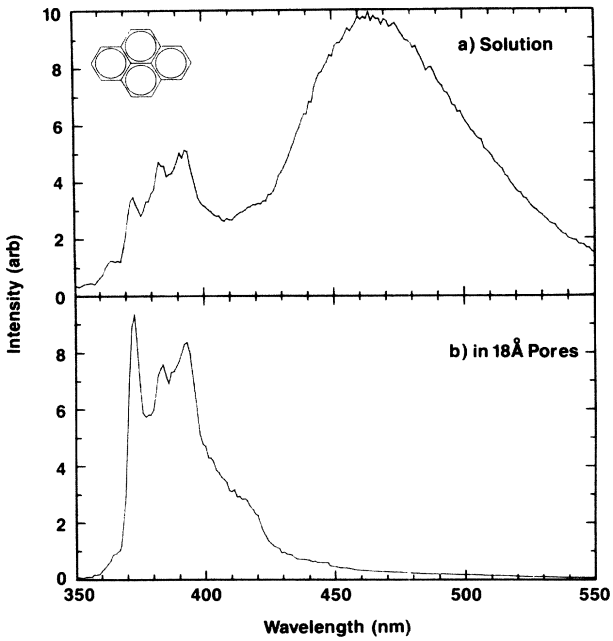

FIG. 3. (a) Fluorescence spectrum of 8 mM isopropanol solution of pyrene excited at 313 nm. (b) Spectrum of pyrene confined in 18-Å-wide superlattice micropores prepared as in Fig. 2.

tures, the surface was cleaned by a semiconductor cleaning procedure[12] which removes any organic residue. The sample was immersed in isopropyl alcohol as a final step before being dipped into a cyclohexane solution of the aromatic to be adsorbed. This process terminates the surface of the pores with alcohol groups, which help to insulate the aromatics from the effects of any reactive groups. This alcohol liner occupies roughly 3–5 Å on each side of the micropore. For this reason we estimate the actual size of the opening to be ~10 Å less than the original layer thickness (which we take below to be the pore width). The total uptake was determined by comparison of the fluorescence intensity to standards, or by optical measurement of the depletion of molecules from the solution. In most cases the micropores were calculated to be within a factor of 2 of being completely filled with aromatic. The fluorescence spectra did not change dramatically when taken under vacuum (to eliminate oxygen quenching) as well as when the sample had been dehydrated in vacuum at 100°C.

The adsorption process was observed to be independent upon both the pore size and the molecular size. No adsorption was observed for micropores with an original oxide width of 8 Å, because of the space taken up by the alcohol liner. Pores 18 Å wide were observed to absorb flat aromatics such as durene, anthracene, pyrene, or perylene quite readily but to exclude larger molecules such as rubrene. Rubrene is an eight-ring aromatic having phenyl groups which stick out of the plane of the nucleus. We believe that this three-dimensional character keeps the molecule from fitting into 18-Å pores.

Molecules were adsorbed by immersion in dilute (~0.05 mM) cyclohexane solution of pyrene, which left aromatics on the surface of the structure as well as in the micropores. This surface pyrene, which gave dimer emission (to be discussed below), could be removed preferentially by rinsing in pure cyclohexane. This increased the monomer/dimer ratio, indicating that the monomer emission shown in Fig. 3(b) is from adsorbed molecules.

Surface pyrene could also be removed by an oxygen milling of the microstructure. These oxygen ions selectively remove organic material, but the adsorbed molecules are protected by the superlattice. Milling for 10 sec (500 eV, 0.3 mA/cm^2) removed any surface molecules; the total fluorescence intensity decreased somewhat and the monomer/dimer ratio increased. Further milling had little effect on the fluorescence, confirming the protection of adsorbed molecules.

These micropores could be cleaned and filled with aromatics repeatedly. The process of wetting and drying sometimes leads to the collapse of the microstructure (the preliminary stages of this process are visible on the left side of the post in Fig. 2). To avoid these problems, we used an entirely wet-sample preparation procedure. Hydrofluoric acid was used to etch out the silicon oxide layers[13] in a-Si:H/a-SiO_x:H multilayers. This structure was then cleaned and dipped in the aromatic solution as before, but without our ever allowing the surface to dry. This process allows the adsorption of molecules without exposing the microstructure to surface tensions.

The fluorescence of polynuclear aromatics such as pyrene can be a very sensitive probe of their environment. We show in Fig. 3 the spectra of pyrene in an isopropanol solution and confined inside 18-Å micropores. These spectra can be separated into two parts[14]: monomer

emission below 420 nm and excimer fluorescence at longer wavelengths. The monomer emission is from isolated molecules and shows vibronic fine structure which can be used to estimate the environment polarity.[15] Band 1 at 373 nm is the 0-0 vibronic band, which would be forbidden under centrosymmetric conditions. The ratio between this band 3 at 385 nm has been shown to be correlated with solvent polarity in a large number of weak pyrene solutions. Pyrene molecules in micropores showed I_1/I_3 ratios between 0.9 and 1.2, depending on the slot width. A dilute isopropanol solution had $I_1/I_3=0.98$, while nonpolar solvents such as cyclohexane have $I_1/I_3<0.6$. Thus, the emission observed from adsorbed molecules [Fig. 3(b)] is consistent with the polarity expected from the alcohol liner.

Figure 3 also shows variations in the relative strength of excimer and monomer emission. The broad excimer band [Fig. 3(a)], peaking at 460 nm, is due to dimerization of two molecules upon the excitation of one of them. The two molecules lower their total energy by overlapping their π orbitals. The excimer emission from pyrene solutions becomes stronger relative to the monomer emission as the concentration is increased, because of the greater probability of an intermolecular collision.[14] Microcrystalline pyrene shows a similar emission due to very strong molecular interactions, although this is not truly an excimer because the molecules are also associated in the ground state. The spectrum of pyrene in superlattice micropores [Fig. 3(b)] shows virtually no excimer emission. This result demonstrates that the confined molecules are too immobile to form dimers within the radiative lifetime, even though this would lower their total energy. The slots of Fig. 3(b) have an opening (~8 Å between the alcohol liners) less than the length of a pyrene molecule, so that free molecular rotations are expected to be severely restricted. This behavior was not observed on any control samples, such as textured superlattices which were not etched to form micropores.

Fluorescence spectra of molecules confined in a series of micropores with different widths are shown in Fig. 4. The aromatic used in these experiments was 1,10-*bis*(1-pyrenyl)decane, shown in the inset. This molecule consists of two pyrene chromophores connected by a decane chain. Excimer emission is observed from this molecule even in dilute solution, because there is always another pyrene chromophore ~10 Å away.[16] This allows us to confirm the process of dimer formation without concerns about the concentration of molecules inside the pores. In 40-Å pores, the fluorescence consists entirely of excimer (or dimer) emission. As the slot width is decreased the strength of the monomer emission increases until it dominates the spectrum for 12-Å pores. This dramatically illustrates the confining effect of the walls upon the molecular properties.

The long-wavelength emission we observed is consistent with ground-state associated molecules. The excitation spectrum of the 40-Å sample, for instance, was very similar to that of solid pyrenyl-decane. The sample could be excited with light between 350 and 390 nm, consistent only with molecules which are preassociated. We also measured the time dependence of the fluorescence to determine the dynamics of excimer formation. If excimers form after excitation, then the fluorescence intensity will rise at first, indicating the time required for two molecules to diffuse together. The 450-nm emission of the 24-Å sample in Fig. 4 peaked within the experimental rise time (<100 psec) after excitation, again indicating preassociated molecules. Pyrene molecules do not preassociate in solution, but this is known to occur inside silica gels[17] and zeolites.[18] We believe that pyrene in our wide pores is forming similar ground-state complexes.

Our data show that pores smaller than ~20 Å are too small for these ground-state dimers to form. About half of this space is taken up by the alcohol liner; the remainder is too small for the free rotation of a pyrene

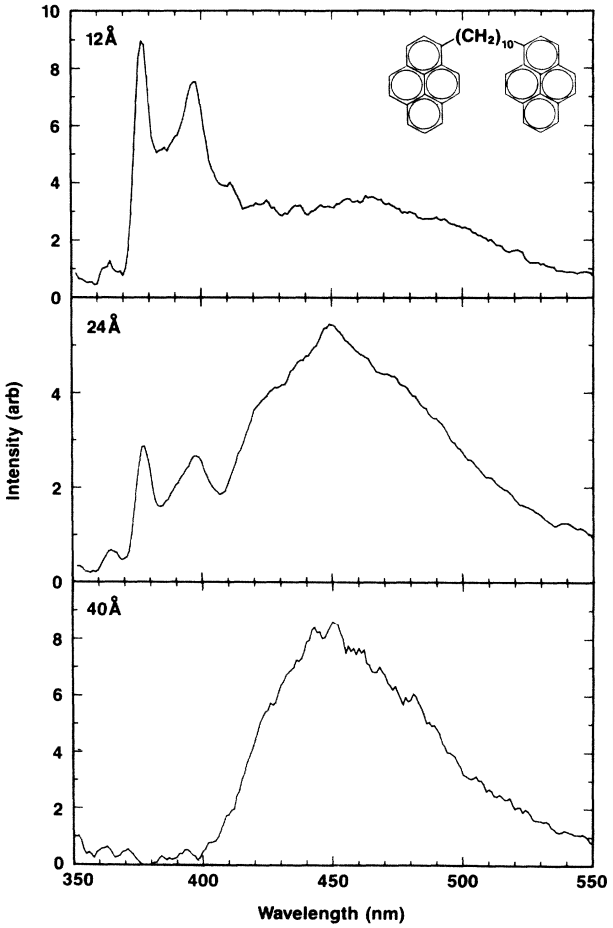

FIG. 4. Fluorescence spectra of di-pyrenyl decane confined in micropores prepared by use of an HF etch on *a*-Si:H/*a*-SiO_x:H superlattices of different layer thicknesses. Each spectrum is the average of several spots on a sample wich was oxygen milled to remove surface pyrene.

chromophore. Presumably molecules in these pores are tied up in the liner in a way which makes associations between them energetically unfavorable. Larger pores have adsorbed molecules well removed from the surface which are free to associate, so that the dimer emission increases with the slot width. We observe that the dimer/monomer ratio increases faster than linearly with the slot width, so that the 40-Å pores have virtually no monomer emission. This is perhaps indicative of an energy transfer process from monomers near the walls to associated molecules.

In conclusion, we have prepared molecular-scale microstructures which exhibit size-selective absorption of aromatic hydrocarbon molecules. Because of the control over pore size and composition, these materials are ideal model systems for the study of molecular dynamics and chemistry occurring in confined spaces. We have absorbed pyrene into pores as small as 12 Å. The fluorescence spectrum is strongly dependent on the pore size. We observe that pyrene dimers do not form in pores smaller than 20 Å.

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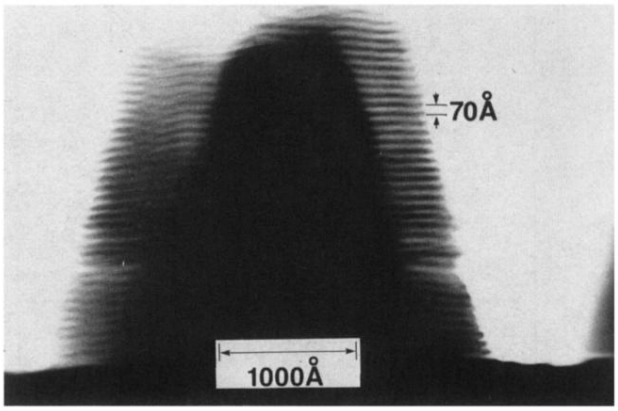

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