ADVANCED
MATERIALS

Tailoring Semiconductor Crystals to Atomic Dimensions**

Molecular Beam Epitaxy
GaAs Thin Films
Film Growth Dynamics
Quantum Wells/Wires
Superlattices

By Bruce A. Joyce*

This article provides an introduction to the growth by molecular beam epitaxy (MBE) of semiconductor structures which have dimensions of the same order as interatomic distances in solids. The basic process technology is first described, followed by a brief account of surface reaction mechanisms involved in the growth of GaAs from an atomic beam of Ga and molecular beams of As_4 and As_2.

From the study of growth dynamics using electron diffraction techniques it is shown how reduced dimensionality structures can be grown and some indication is given of the effects of quantum confinement on material properties. Finally, some recent modifications of MBE based on flux interruption are described.

1. Introduction

It has become possible to fabricate semiconductor structures having dimensions of the same order as interatomic distances in solids. They are usually referred to as low dimensional systems. The movement of electrons in these structures is constrained because their dimensions are less than the electron wavelength and as a result they exhibit properties very different from those of the bulk material. The electronic confinement can be in one, two or three dimensions to produce layers, wires and dots respectively and the effects are already being exploited in novel electronic and opto-electronic devices, of which the quantum well laser is perhaps the best known example.

In this short article I will describe the technique of molecular beam epitaxy (MBE) which is one of the two major fabrication methods used to prepare low dimensional systems, indicate how the necessary levels of control and understanding have been achieved, and illustrate some of the reduced dimensionality structures which can be grown directly.

2. Molecular Beam Epitaxy (MBE) – The Process

The fundamental principles of MBE were established over twenty years ago, first for silicon and subsequently for III–V compounds such as gallium arsenide (GaAs). The subject has been extensively reviewed.[1–5] In this technique atomic or molecular beams are formed from Knudsen effusion cells and allowed to impinge on to a heated substrate under ultra high vacuum (UHV) conditions of $< 10^{-10}$ torr. If the conditions are correct a single crystal epitaxial film grows on the substrate, which is typically a single crystal semiconductor wafer approximately 5 cm in diameter. The cells are maintained at room temperature for gaseous sources or heated to produce an adequate vapor pressure for solid phase source material. Typical source pressures are in the range of 10^{-2} to 10^{-3} torr, which allows operation in the molecular flow, or collision-free regime, so that the first collision of a beam molecule is with the substrate. Under these conditions the molecular flux at the substrate is given by:

$$J_i = [a p_i / \pi d^2 (2 \pi m_i k T)^{1/2}] \cos\theta \tag{1}$$

where J_i is the flux per unit area at a distance d from the source, which has an orifice of area a and contains molecules (atoms) of mass m_i having an equilibrium vapor pressure p_i at a temperature T K. θ is the angle between the beam and the substrate surface normal. The flux is regulated by a fast-acting shutter operating in front of each aperture.

A microcomputer is used to controll cell and substrate temperatures and all of the shutter operations, enabling any predetermined growth sequence to be achieved. Since the beams are neutral and collimated (by the aperture geometry) they are necessarily divergent and usually non-axial with respect to the substrate. To obtain uniform growth rate and composition (in the case of alloy films) over a large substrate area, the substrate stage is rotated at speeds between 0.03 and 2.0 Hz. For the growth of high quality films a substrate surface free of crystallographic and other defects and clean on an atomic scale (< 0.01 monolayers (ML) of impurities) must be prepared. This usually involves free etching by an oxidative process which removes any carbon and leaves the surface covered with a protective volatile oxide which is subsequently removed by thermal desorption in the vacuum chamber.

Experimental systems which can provide the required levels of control have become rather complex, but Figure 1 illustrates schematically the important features. The basis is

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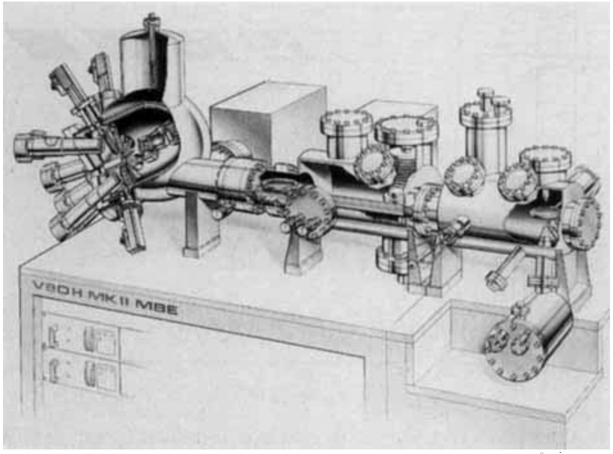

Fig. 1. Schematic illustration of an MBE system for the deposition of III–V compounds.

a two or three chamber stainless steel UHV system, usually ion- or cryo-pumped and incorporating large areas of liquid nitrogen cooled panels. An interlock system to enable the substrate to be introduced into the growth chamber without breaking the vacuum is essential if films having high quality electrical and optical properties are to be prepared.

In situ analytical facilities usually include a quadrupole mass spectrometer for residual gas analysis and a reflection high energy electron diffraction (RHEED) arrangement for assessment of surface structure and growth dynamics (see section 4). This consists of a 10–50 keV electron gun and a fluorescent screen, using a forward scattering geometry with the electron beam at a very shallow angle (1–3°) to the substrate surface. In addition, an Auger electron spectrometer may be incorporated to determine surface composition and purity. Some or all of these analytical facilities may be housed in a separate analysis/preparation chamber mounted between the sample insertion interlock and the growth chamber.

In the remainder of this article I will concentrate on films of III–V compounds, principally GaAs prepared from solid (elemental) sources, since most of our understanding of growth mechanisms and most areas of application relate to these materials, but the same basic principles apply to silicon, germanium and II–VI compounds.

3. MBE of III–V Compounds – The Basic Chemistry

The source materials used are usually elemental, and all of the group III elements produce monoatomic beams. Group V sources are rather more complex, since direct evaporation produces tetraatomic molecules (P_4, As_4, Sb_4), but dimeric molecules can be obtained by passing the tetramer flux through a high temperature stage at the front of the Knudsen cell. Dopants used are beryllium for p-type and silicon for n-type, both of which evaporate as monomers.

Growth is initiated by bringing the substrate to the appropriate temperature (typically in the range 500–700 °C) in a beam of the Group V element to prevent thermal dissociation and then opening the shutter of the group III element source. A typical growth rate is 1 $\mu m h^{-1}$, which corresponds approximately to 1 $ML\,s^{-1}$, or a flux of 5×10^{14} atoms $cm^{-2}\,s^{-1}$. The group V element flux may be between three and ten times greater, but the growth rate is entirely determined by the group III element flux.

The experimental arrangement of MBE is unique amongst epitaxial thin film preparation methods in that it allows direct in situ reaction kinetic measurements to be made using the technique of modulated beam relaxation spectroscopy (MBRS). The basic experiment is very simple; a neutral, thermal atomic or molecular beam is directed at a substrate surface and the desorbing flux detected mass spectrometrically. The problem of distinguishing between background signals and those produced by desorbing species is solved by (mechanically) modulating either the incident beam or the desorbing flux and examining the mass spectrometer signal for a correlated response. By correct choice of data acquisition and signal processing methods[6] it is possible to evaluate a wide range of kinetic parameters, including (i) thermal accommodation coefficients of molecules interacting with the surface, i.e. the nature of kinetic energy exchange processes between the surface and the incident species (ii) surface lifetimes and the energies of binding states (iii) sticking coefficients, or residence times which are long compared to the modulation frequency and (iv) orders of chemical reactions.

A good example of the power of the technique comes from its application to the interaction of Ga and As_4 beams on a GaAs(001) surface to form GaAs.[7] The presently accepted model for this is shown in Figure 2. The As_4 molecules are first adsorbed into a weakly bound mobile precursor state, in which the activation energy of migration is approximately 0.25 eV. An activation energy of desorption of ≈ 0.4 eV can be determined from the temperature dependence of the sur-

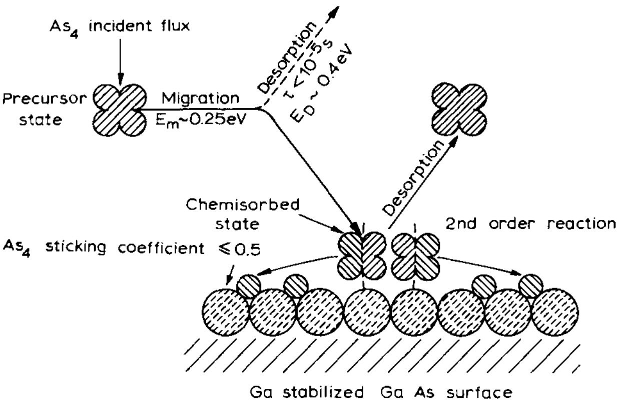

Fig. 2. Model of the growth chemistry of GaAs from molecular beams of Ga and As_4.

face residence time of an As_4 molecule. A crucial finding is that the sticking coefficient of As_4 never exceeds 0.5, even when the Ga flux is much higher than the As_4 flux, or when the surface is completely covered with a monolayer of Ga atoms (as in Fig. 2). Furthermore, the desorption rate is second order with respect to the incident flux. These results are explained by postulating a pairwise dissociation of As_4 molecules chemisorbed on adjacent Ga atoms, so from two As_4 molecules four As atoms go to form GaAs, while the remaining four desorb as an As_4 molecule. By contrast, in growth from As_2 the basic process for As incorporation is simple first order dissociative chemisorption on surface Ga atoms.[8]

These models are well over ten years old, but they have received some very recent experimental support from *Tsao* et al.[9] These workers also found a maximum As_4 sticking coefficient of 0.5, at which point the surface reconstruction changed from As-stable to Ga-stable. In addition, they were able to show that the chemical reaction was not the rate determining step in the growth of a GaAs film, which is an important factor in the discussion of growth dynamics (see section 4).

4. The Dynamics of Film Growth

Before embarking on a discussion of growth dynamics it is important to establish the basic concepts of the surface structure of GaAs, which can be monitored by the in situ RHEED facility. In general, semiconductor surfaces either relax by bond rotation on reconstruct, i.e. display a lower symmetry than that produced by a simple termination of the bulk lattice. In III–V compounds the form of the reconstruction is related to surface composition and stoichiometry, which can be illustrated by the GaAs(001) surface. It is a polar orientation and is ideally terminated by a complete layer of Ga or As atoms, but in practice it forms a series of surface structures, ranging from the Ga-rich 4 × 2, though an intermediate 3 × 1 to an As-stable 2 × 4, where (n × m) relates the surface unit cell to that of the bulk (1 × 1) and indicates the increase in the periodicity in two orthogonal ⟨110⟩ directions at the surface. In addition to displaying the surface symmetry the RHEED pattern can also be used to evaluate surface morphological properties such as the presence of steps, facets, antisite disorder etc.[10]

A further and extremely important application of RHEED is the direct in situ study of film growth dynamics. This has been made possible by the discovery and development of the RHEED intensity oscillation technique.[11, 12] The primary observation is that damped oscillations occur in the intensity of all features of the RHEED pattern immediately following the start of growth. Typical results for the growth of GaAs and AlAs(001) oriented films on GaAs(001) substrates are shown in Figure 3, taken using the specular spot on the 00 rod. The steady state period corresponds precisely to the growth of a single molecular layer, i.e. a complete layer of Ga(Al) + As atoms, equivalent to $a_0/2$ in the [001] direction.

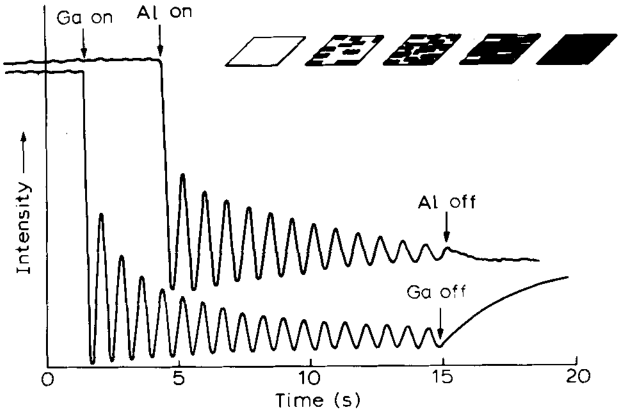

Fig. 3. Intensity oscillation of the specular beam in the RHEED pattern from AlAs and GaAs(001) 2 × 4 surfaces during growth. Inset shows the growth of a molecular layer in a two-dimensional mode.

The feature common to all explanations of this oscillatory intensity response is that it occurs as a direct result of the changing surface topography associated with a layer-by-layer (two-dimensional) growth mode. On the basis of 2-D growth and a single scattering diffraction process it is a straightforward matter to construct a growth model which accounts for the RHEED results. We will deal with the specular spot for simplicity, but similar arguments can be applied to all features. If we relate intensity changes with surface roughness effects on an atomic scale, we can assume that the equilibrium surface is smooth, corresponding to a high specular intensity. When growth commences, 2-D centres are formed randomly on the surface, leading to a decrease in specular intensity (i.e. an increase in diffuse scattering). This is the expected result for a single scattering process, since the wavelength of the electrons is typically 0.1 Å whilst the GaAs monolayer step height is 2.83 Å i.e. the wavelength is more than ten times smaller than the size of the scattering centers, thus producing diffuse scattering. This will be a maximum at half-layer coverage ($\theta = 0.5$) and a minimum at the start of each layer ($\theta = 1$). The development of a monolayer is illustrated in the inset to Figure 3. In fact this model is greatly oversimplified, because electron diffraction is a multiple scattering process, but the basic tenet is correct; the oscillatory response is a manifestation of a layer-by-layer 2-D growth mode which implies significant adatom migration on the surface. In reality an intensity maximum seldom corresponds to monolayer completion because its position in the monolayer depends strongly on diffraction conditions (azimuthal and polar angles). Fortunately conditions can be chosen which ensure correspondence between intensity maxima and monolayer completion. The complexities introduced by diffraction effects have been treated extensively elsewhere[12] and need not concern us further here. The decay of the oscillations is particularly important, however, since it represents a change of growth mode from 2-D nucleation to step propagation. As a result of the growth front becoming distributed over more than one layer, brought about by a second layer starting before the previous one is complete, a steady state terrace width, or step distribution is eventually established. This occurs when the mean step separation equals the surface migration distance of the group III adatoms. Under these conditions there are no intensity oscillations since statistically the surface morphology does not change during growth.

These growth mode changes which occur as a consequence of the surface migration of adatoms can be exploited in a rather simple way to establish quantitative data for the migration processes.[13] The method involves the use of a vicinal surface, which means preparing a substrate so that its surface plane is a few degrees away from a singular surface, i.e. a surface with an exact low index orientation, (001) say. To minimize its free energy, a surface of this type will break up into a formation of exact (001) terraces separated by monomolecular steps (of height $a_0/2$ in the case of III–V compounds). The mean step-free terrace width l, is given by $l = a_0/2 \tan\alpha$, where α is the angle of misorientation. As an example for $d \approx 2°$, $l \approx 80$ Å. If the migration length of the group III element is λ, for $\lambda > l$ the step edge will act as the major sink for migrating adatoms and there will be no two dimensional (2-D) growth on the terrace. Since RHEED intensity oscillations occur only as the result of 2-D growth, they will be absent for this growth mode. If, however, growth conditions are varied to the point where $\lambda < l$, 2-D growth will be re-established on the terraces and oscillations will be observed. It is consequently comparatively straight forward to study λ as a function of growth conditions. It must be emphasized, however, that in the present context surface migration refers to the transport of group III adatoms in a weakly bound precursor state before their final incorporation in a lattice site; it is migration related to growth, not surface dissociation.

Ideally, the measurements should be performed by systematically varying the extent of misorientation and hence terrace width, but in practice it is simpler to use a single substrate with a fixed misorientation and vary the migration length by changing growth parameters. A typical data set obtained by varying the substrate temperature at fixed As_2 and Ga fluxes is shown in Figure 4. The inset illustrations demonstrate the changing growth modes as the temperature changes. Clearly, as the temperature rises the migration length increases to the point where it equals the terrace width, and the RHEED intensity oscillations disappear. If surface migration is assumed to be isotropic, it is possible to determine values of the migration coefficient D_0 and the activation energy E_d using the relationships:

$$\lambda^2 = 2\,D\tau \tag{2}$$

and

$$D = D_0 \exp(-E_d/kT) \tag{3}$$

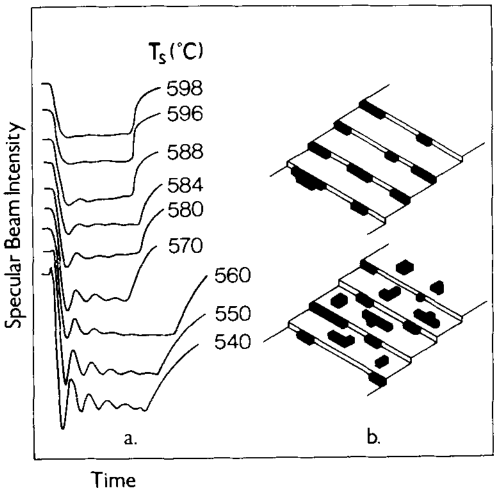

Fig. 4. Data set showing the transition from oscillation to constant response in the RHEED specular beam intensity as a function of substrate temperature, with constant gallium flux, for the growth of GaAs. Inset illustrates layer-by-layer and step propagation modes on the terraces formed from the vicinal surface.

Here λ is the mean displacement (terrace width), D the migration coefficient at a temperature T and τ the surface lifetime in the precursor state. There are some detailed analytical difficulties, but the basic principles appear to be valid.

5. Quantum Wells, Superlattices and Quantum Wires

We have seen that the fundamental growth mode on a singular surface is layer-by-layer and this enables quantum wells and superlattices to be grown. In a quantum well, a layer of one material, say GaAS, is sandwiched between two layers of material of greater band gap, say (Al,Ga)As, a III–V alloy in which some fraction of Ga is substituted by Al. More complex alternating structures are known as multiple quantum wells (MQWs). When the layers are sufficiently thin (typically < 20 Å) to allow electron coupling between them, the structure is referred to as a superlattice. Detailed consideration of the transport and optical properties of such structures are outside the scope of this article, but an excellent review has been written by *Kelly* and *Nicholas*.[14] It will perhaps be useful however to discuss briefly one example here. In semiconductors the recombination of electrons and holes causes the emission of radiation. In a quantum well structure the energy of this radiation increases (the wavelength decreases) as the well thickness is reduced. This is a quantum shift brought about by the confinement of the electrons in the well to two dimensions. The actual wavelength of emitted light is a function of the well width and this has been used to fabricate MQW lasers with emission characteristics quite different from those based on the equivalent bulk materials.

Some idea of the perfection with which two dimensional structures can be grown may be obtained from electron microscopy and this is illustrated in Figure 5. This is a cross sectional transmission electron micrograph (TEM) of a GaAs-AlAs superlattice composed of alternate layers each 3 ML (8.5 Å) thick. It is evident that averaged over the thickness of the cross section, interfaces on a scale of < 1 ML can be produced. Similar conclusions can be drawn using X-ray diffraction and photoluminescence techniques.

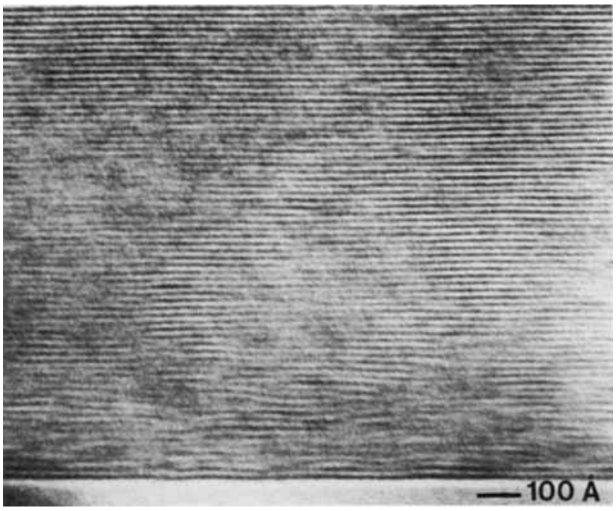

Fig. 5. Transmission electron micrograph of a GaAs (3 ML)/AlAs (3 ML) superlattice.

Quantum well wires are low dimensional structures with quantum confinement in two dimensions. Most attempts to fabricate them have relied on high resolution lithography, but the lateral dimensions achieved have been rather too large to produce significant separation of sub-band energies. A new approach has been made possible by control of the growth mode on vicinal planes, following the principles discussed in section 4. By restricting growth to the step propagation mode and growing alternate fractional monolayers of, say, GaAs and AlAs on a GaAs(001) substrate tilted typically 2° towards (110), vertical columns of GaAs and AlAs can be grown on the terraces, which are ≈ 80 Å in width.

There is already evidence[15,16] of some success in the growth of these structures, although it is clear that as yet they are far from ideal. Simulation studies indicate that poor quality at low substrate temperatures results from a significant amount of two-dimensional cluster formation due to restricted surface diffusion, whilst high temperature degradation is brought about by enhanced thermal fluctuations in the step edge structure.

6. Growth Process Modifications

Finally, we may consider some recently developed modifications to the growth process, which were introduced with the idea of growing more "perfect" interfaces in heterojunctions, quantum wells and superlattices, i.e. maximizing areas of single composition in the interface plane, or minimizing the number of layers normal to the plane in which compositional variations occur. They all rely on interruption of one or other or both (anion and cation) fluxes.

If growth is stopped by shutting off the group III element flux whilst maintaining constant the substrate temperatures and group V element flux, the intensity of the specular spot in the RHEED pattern recovers almost to its pre-growth value, provided correct diffraction conditions are chosen. The "recovery" or relaxation, occurs in two stages (fast and slow) and obeys an expression of the form:

$$I = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \tag{4}$$

where τ_1 and τ_2 are the temperature dependent time constants of the fast and slow stage respectively. It seems probable that during the fast stage singly coordinated atoms on the peripheries of two dimensional growth centers break away to reform into more highly coordinated sites. The slow step then results from adatom clusters evolving to form the maximum number of nearest neighbor bonds.

This is the basis of the simplest modification, known as interrupted growth,[17] where the shutter controlling the cation flux is closed for periods of up to 60 s. This results in a lower step density and is more successful for lower binding energy, faster diffusing species, and it is also important for the interruption to occur close to monolayer completion. The other two modifications, known as atomic layer epitaxy (ALE)[18] and migration enhanced epitaxy (MEE)[19] both involve periodic interruptions of each flux during growth. It is claimed that as well as improving interface morphology, both techniques produce high quality material at lower substrate temperatures than is possible by conventional growth, but it is a claim which remains to be fully substantiated. It appears that both ALE and MEE depend on rapid relaxation during a short interruption period which occurs very close to monolayer completion.

It is reasonable to conclude that semiconductor structures of atomic dimensions, at least in one direction, can be reliably fabricated using MBE or one of its related alternatives. Some success has been achieved in control over two dimensions on the same scale, but much work remains to be done before successful exploitation can be claimed. Control over all three dimensions is still very much in the "ideas" stage.

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Structure-Directed Synthesis of New Organic Materials**

Unnatural Products
Molecular LEGO
Solvent Sensors
Zeolitic Macropolycycles
Diels-Alder Reactions

By Franz H. Kohnke, John P. Mathias, and J. Fraser Stoddart*

1. Preamble

The time has now been reached when the chemist can make almost anything the living world has produced. Natural product synthesis has dominated the conceptual advances in synthetic organic chemistry for more than a century now. Yet, although the deep significance and fundamental importance of natural products and the life processes that sustain and characterize them are clear, they are arguably only an infinitesimally small part of the chemical scene. Compounds which are wholly unnatural comprise an infinite variety of structures which can only be conceived and constructed thanks to the knowledge, imagination, and expertise of the chemist. The reasons for making unnatural products come from many quarters – they include evaluating chemical theories, both old and new, synthesizing exotic compounds, which, more often than not have symmetry appeal, and preparing materials with some particular structural form that might perform some highly desirable physical, chemical, or biological function.

The manufacture and manipulation of structures at a molecular level raises[1] "the possibility of maneuvering things atom by atom." The prospect is one of performing physical feats on a truly microscopic scale. The question is how to construct advanced materials that express their properties at a molecular level and then to gain access to these properties, i.e. how do we make molecules and speak to them?

Recently, rigid molecular lines or strips, with nanometer scale dimensions and composed of polyacenequinone units, have been prepared[2] by repetitive Diels-Alder reactions. Their synthesis is attractive because they could provide a range of new materials capable of forming organized monolayers and molecular electronic devices of different sorts. Artificial cell bilayer membranes, and molecular barriers and sensors all rely[3] upon the formation of surface structures with the appropriate electronic characteristics. The prospect[4] that the parent polyacenes and their cyclic analogs – the cyclacenes – constitute materials with "the possibility of possessing interesting condensed phases including high temperature superconductivity and ferromagnetism" is particularly tantalizing.

Although synthetic strategies based on a repetitive Diels-Alder methodology, involving bisdienes and bisdienophiles,[5] have much to commend themselves in the synthesis of ladder polymers, there is a need to avoid ill-defined mixtures of compounds containing molecules of differing molecular weights and different stereochemistries that are not particularly amenable to purification by chromatography or by any other means.

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