Semiconductor Surface Studies

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Introduction

Understanding the properties of the surfaces and interfaces of solids is of extreme importance both from technological and academic points of view. The advent of ultrahigh vacuum technology has made microscopic studies of well-characterized surface and interface systems possible. The way atoms move to reduce the energy of their surface, the number of layers of atoms involved in this reduction, the electronic and vibrational states that result from this movement, and the final symmetry of the surface or interface region are all of utmost importance in arriving at a fundamental and microscopic understanding of the nature of surfaces, chemisorption processes, and the initial stages of interface formation.

The theoretical problems associated with these systems are quite complex. However, we are currently at the forefront of solving the properties of real surface systems. In particular, we are continuing our efforts in developing new techniques for calculating the total ground-state energy of a surface system from "first principles," so that we can provide accurate theoretical predictions of surface geometries and behavior. Our efforts in this program have concentrated on exploiting this computational advance in order to deliberately design a novel interface system from first principles.

1. Computational Design of Novel Optical Material

Sponsors
Joint Services Electronics Program
    Grant DAAH04–95–1–0038
Office of Naval Research
    Contract No. N0001-94-1-0591

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In the optoelectronics industry, great efforts have been devoted to monolithically integrate electronic materials with optically active materials. As the sizes of electronic devices continue to shrink and the usage of optical communication continues to grow, monolithic integration becomes increasingly desirable and necessary. Various different approaches have been suggested, each with its own problems.

One very natural approach is to heteroepitaxially grow optically active materials, such as GaAs for example, directly on top of Si. However, there are two basic problems facing epitaxial growth of these optical materials on Si substrates. Firstly, heteropolar semiconductors, e.g., III-V's and II-VI's, are polar when grown along the (001) direction. This causes a polarity mismatch with the underlying group-IV substrate. Secondly, most existing optical materials and their alloys do not match lattice constant with Si. In Fig. 1 we plot the band gaps and the lattice constants for

conventional semiconductor alloys that are currently used for optically active devices. The III-V alloys shown in Fig. 1 that exhibit band gaps matching the operating wavelength of optical fibers (~1.5 microns) have lattice constants about 8% larger than that of Si. Therefore, it is impossible
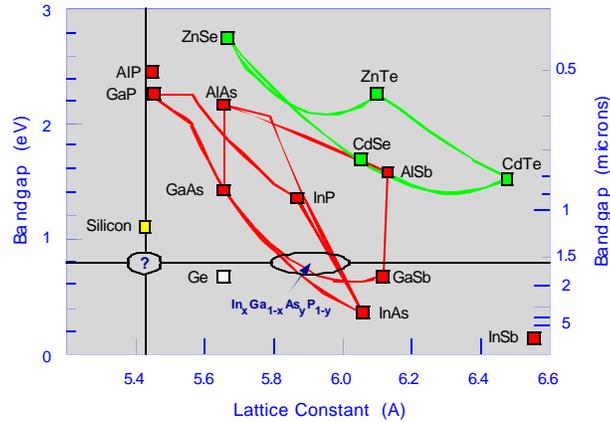

Figure 1. Band gaps and lattice constants for various traditional semiconductor materials. The III-V's are shown as red squares, and the II-VI's are shown as green squares. The color-shaded areas denote possible alloyed materials. The InxGa1-xAsyP1-y alloy has a bandgap near 1.5 microns and is the current industry standard. The large lattice constant mismatch with Si prohibits monolithic integration. An ideal material would have a lattice constant and bandgap lying in the region containing the question mark.

to grow these alloys defect free on Si substrates. The polarity mismatch and the lattice mismatch make it exceedingly difficult to create optoelectronic integrated devices using heteroeptiaxy.

The goal of this project is to exploit the predictive power of *ab initio* calculations to deliberately design a novel compound semiconductor that: (1) resolves the polarity-mismatch problem; (2) matches the lattice constant of Si; (3) is an optically-active material; and (4) possesses a gap near 1.5 microns.

Let us begin by considering the polarity mismatch problem. The typical interface of a III--V compound on a Si(100) substrate is illustrated schematically in the left panel of Fig. 2.. Each atom makes four bonds with its four neighbors. As is clear from the illustration, in order to satisfy the two-electron-per-bond counting rule, half an electron per first-layer group-V atom must be
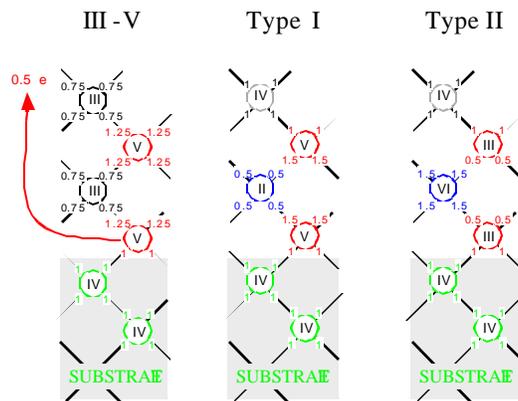
redistributed to the outer surface of the structure, thus creating a long-range electric field that accounts for the polarity mismatch.

Our solution to this problem is to reduce the valency of the second layer atoms. As is shown in the center panel of Fig. 2., the valency of the second layer atoms is reduced by one to accommodate the extra electrons from the neighboring group-V atoms of the first layer and the third layer. In doing so, we also need to increase the valency of the fourth-layer atoms by one to satisfy the total electron counting requirement. This layering process can then be repeated without generating a long range field. Similarly, an alternative solution is to start the epitaxial layering with group-III atoms and increase or decrease the valencies of the group-V layers, as is illustrated in the right panel of Fig. 2.. In both cases, the charge-mismatch problem of the interface is resolved.

In effect, we have created a class of "pseudo" III--V materials, with either the group-III element replaced by a combination of group-II and group-IV elements, or the group-V element replaced by a combination of group-IV and group-VI elements. These two possibilities will be denoted as Type I and Type II materials, respectively.

It should be emphasized that there may be more than one component to any of the three groups. For example, given group-II atoms Zn, Cd, group-IV atoms Si, Ge, and group-V atoms P, As, one could form the compound

… Si–P–Zn–As–Ge–As–Cd–As–Si …

Moreover, combinations of the two types of materials may also be considered in epitaxial growth:

substrate : Type I/II : Type I/II :

Interestingly, Type I materials have the same chemical formula as the naturally occurring Chalcopyrite materials. However, the atomic structure is different. The alternating layers of group-II and group-IV elements in Chalcopyrites are intermixed, which make layer by layer heteroepitaxial deposition difficult and also create the same polarity problem as the III--V's.

With the polarity-mismatch problem resolved, the next step is to identify candidates with lattice constants matching that of Si. Since the number of possible choices of atom types and Type I/II layered sequences is enormous, the effort to build and test the potential candidates experimentally would be formidable. In contrast, first-principle calculations on computers can go through many possibilities quickly. We proceed by searching the simple materials first and gradually increasing the complexity involved.

As a starting point, we use data on the tetrahedral-covalent radii of elements to get the approximate lattice constants of various materials. (Detailed calculations later show that they could have an error as large as 4%.) Nonetheless, these estimated lattice constants are valuable in narrowing the search space. According to these estimates, there are 34 Type I and 41 Type II materials with lattice constants that fall within 10% of the Si lattice constant. We start by concentrating on a sampling of those within 3%, and use *ab initio* total energy methods to calculate more accurate lattice constants.

The total electronic energy within the local-density-approximation (LDA) is minimized using the preconditioned conjugate-gradient algorithm. The LDA calculations are performed with the Perdew-Zunger parameterized exchange-correlation energy and the Kleinman-Bylander separable form of optimized pseudopotentials . For Zn and Cd, nonlinear core corrections are used. The total energy is a function of the lattice constants as well as the basis vectors. The ions are relaxed according to the Hellman-Feynman forces for each given set of lattice vectors. The lattice constant is then located by finding the minimum of the total energy in the lattice vector space. The cutoff energy used in the calculations is $E_c = 20$ Ry except for materials involving first row, for which $E_c = 40$ Ry is used. The LDA method has been proven capable of predicting lattice constants to within 1% of the true values. Once materials with the correct lattice constants are found, their band structures are studied to see if they are direct band-gap materials with the desired gap size. Since LDA methods give poor band-gap results, a much more computationally intensive approach, involving the quasi-particle GW scheme, is used to obtain accurate band-gap information for the most promising candidates.

Formation enthalpies are calculated to investigate if these materials are stable against segregation into equilibrium phases of the elements. The formation enthalpies are found to be typically positive, indicating the materials are stable. In the case of $(ZnSi)_{1/2}As$, it is 0.33 eV per atom. This is only half the value of that of the corresponding Chalcopyrite. Thus, our new material is only meta-stable. The conversion to Chalcopyrite, however, involves second-nearest-neighbor exchange and creation of interstitials. We expect the diffusion barrier to be very high and the process unlikely to occur.

The results of the LDA studies reaveal that there is one structural candidate – $(ZnSi)_{1/2}As$, which has a lattice constant within 1% of that of Si. Unfortunately, it has a small indirect band gap. Indeed, all of the compounds studied have either indirect or marginally indirect (<0.1eV) gaps, except for $(ZnSi)_{1/2}P$ and $In(CS)_{1/2}$. Since $(ZnSi)_{1/2}P$ has a gap that is larger than desired and a lattice constant smaller than that of Si, it is natural to alloy it with a material that has a smaller gap and a larger lattice constant. Although there are several possible choices, we focus on one particular candidate, $(ZnSi)_{1/2}As$. By mixing these two materials, both the lattice constant and the band gap should be closer to the desired values. This mixing is easily done, since the epitaxial layering scheme allows us to use different group-V elements in different layers of one material. This new type of material can be written as $(ZnSi)_{1/2}P_xAs_{1-x}$, where x indicates the relative percentage of phosphorus used.

We studied several alloys with different x values, and established the trend of lattice constant and band gap as x varies. From Fig. 3., it is clear that a good lattice match can be found near x = 0.25, with a lattice constant only 0.08% smaller than that of Si. The results also show that the gap
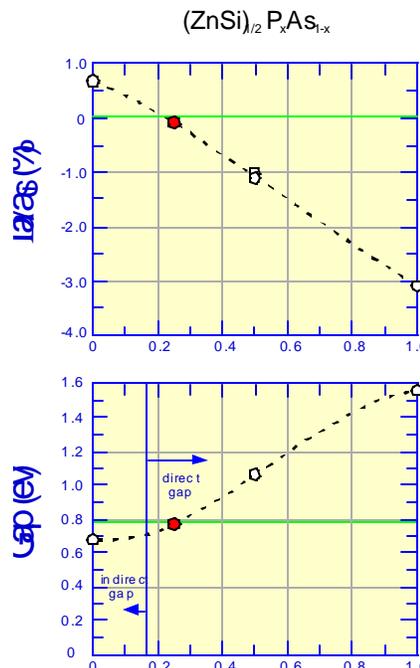
$(ZnSi)_{/2}P_xAs_{1-x}$

is clearly direct, although marginally so, and is about 0.78 eV. This corresponds to 1.59 microns, which is close to the canonical optoelectronics wavelength. Note, the precise value of this gap is not as important as the possibility of tuning it by the appropriate phosphorus concentration. As it stands, the chemical formula of this material is $(ZnSi)_{1/2}P_{1/4}As_{3/4}$. Growth of this new material on a Si(100) substrate could then follow the sequential deposition:

$$As - Zn - As - Si - As - Zn - P - Si$$
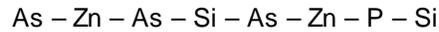
with repetition in this order. This is shown schematically in Fig. 4..

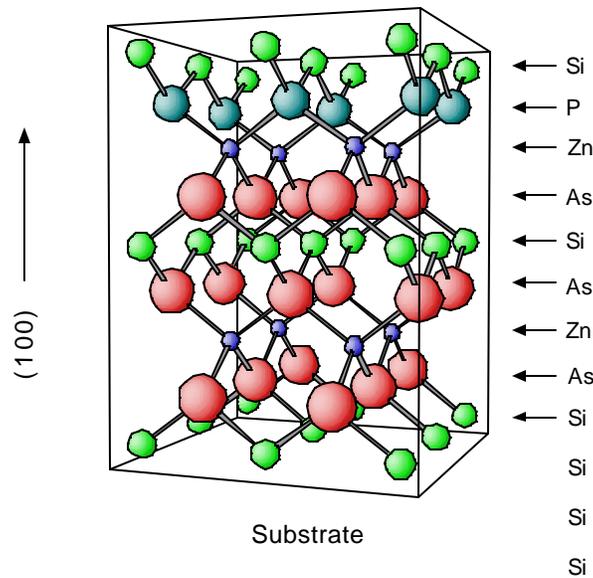Figure 4. An illustration of the crystal structure of $(ZnSi)_{1/2}P_{1/4}As_{3/4}$.

In order to gauge how well the lattice constants continue to match as temperature increases, we can estimate the thermal expansion coefficients from the total energy surfaces for both the new material and Si. The difference in the percentage increase of the lattice constant ($Da / a(T)$) for the two materials is calculated to be less than 0.01% from 0K to 600K, and actually vanishes at 350K. This suggests that thermal expansion will not cause additional lattice mismatch.

Finally, the new alloy material that we have designed will possess a slight dipole moment, due to the difference in chemical properties of phosphorus and arsenic. However, this dipole moment can be eliminated if we invert every other cell in the growth direction, i.e. use a supercell twice as long in the growth direction.

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