these ideas had its controversial period, its convinced opponents, and its apparent experimental failures. It may be amazing how deep scientists' emotions can run in the midst of this process, but, except for the case of Boltzmann, Porter hardly documents that. Nor does he discuss an extraordinarily contentious field, like high-temperature superconductivity.

Finally, I found the brief (four-page) chapter on Blas Cabrera's observation of a single magnetic monopole out of place. Any single observation, no matter how bizarre, allows for too many alternative explanations: pranks, coincidence, inattention, thoughtless mistakes, some anomalous type of cosmic radiation, vermin, et cetera. If Porter needed an example of implausible and controversial observations, there were others available from the same laboratory (free quarks and falling electrons were aberrations of Cabrera's predecessor). To Cabrera's credit, he never oversold his monopole (assuming one accepts publishing as an isolated event).

The "Conclusions" chapter does not suc-

SCIENCE'S COMPASS

ceed in unifying Porter's diverse examples. These suggest that scientists' controversies are not settled by bargaining, compromise, mediations, or bluffing, and that lying and fraud are quite uncommon. Inevitably, there is a right answer, although it may not win politically and its victory may only be recognized after a lot of history. That scientific theories often die only with their advocates is a true, but not new, insight.

Unfortunately, Porter sometimes repeats as fact folklore that is questionable or even wrong. That the effectiveness of the physics community "reached its highest point in the 1920s and 1930s" seems merely the reminiscence of a survivor looking back at his youth. Those years may have been a Golden Age, but there are others: the Standard Model was produced in the 1960s and 1970s by a rather small, tight community; modern condensed matter theory dates from the 1950s and 1960s; modern astrophysics is still growing and, with the advent of the Hubble telescope, may be in its greatest period. Also, in contrast to Porter's claim that "in recent years

most Nobels are for high-powered and expensive experiments," only a quarter of the last 40 physics prizes have rewarded such efforts and, notably, the most recent awards have gone to individual or small group efforts.

Physicists in Conflict suffers from other shortcomings. The writing is often puzzling, leaving one wondering what "this" refers to. The discussions, such as those on kinetic theory and the complex set of ideas about the multiple production of particles, sometimes fail to explain the science.

In summary, stories of conflict in science, or between scientists and the establishment, can be fascinating and enlightening, but I feel that the source materials offer better reading than this collection. Unfortunately, a great book that captures internal conflicts in science has yet to appear.

References

- 1. S. Brush, *Statistical Physics and the Atomic Theory of Matter* (Princeton Univ. Press, Princeton, NJ, 1983).
- I. Langmuir, *Pathological Science*, transcribed and edited by R. N. Hall (General Electric, Schenectady, NY, 1968).

PERSPECTIVES

PERSPECTIVES: SURFACE CHEMISTRY

Reactions on Semiconductor Surfaces

SCIENCE'S COMPASS

Harry E. Ruda

hemical reactions on surfaces are important in many areas of science and technology. On metal surfaces, the electronic states of the surface atoms are spatially extended and can therefore easily be shared with those of reactive species, dramatically influencing the structure of these species as they approach

Enhanced online at www.sciencemag.org/cgi/ content/full/283/5402/646

the surface. In contrast, bonding on semiconductor surfaces is largely cova-

lent, and surface electronic states tend to be spatially localized. Many technologically important processes—epitaxial layer growth, dopant incorporation, and the patterning of semiconductor surfaces by selfassembly, for example—proceed through semiconductor surface reactions. This has important implications for the structural and electronic properties, and thus the performance, of semiconductor devices, particularly nanostructured devices that require high local control over surface properties. In this active and fertile area, recent studies have highlighted the importance of specific surface sites and local response to adsorbed species in surface reactions on semiconductor surfaces.

Understanding of the interactions of species with semiconductor surfaces has been considerably advanced by the now widespread use of scanning tunneling microscopy (STM). STM can probe the spatial extent of electron density on a surface with atomic resolution. Bias-dependent STM studies, in which images are taken at different voltages between the STM tip and the sample, allow the determination of the energy spectra of surface electronic states, and, in special cases, enable discrimination between different chemical species. For example, in the case of GaAs, charge transfer from Ga to As atoms makes the Ga sites visible for positive sample bias and the As sites visible for negative bias. STM can also be used to distinguish different chemical species on more complex semiconductor surfaces, especially in combination with laser excitation.

On metallic surfaces, so-called nucleation-growth and related models have successfully explained a number of molecular adsorption reactions. Key assumptions are (i) relatively high sticking coefficients for the molecules on the surface, (ii) surface diffusion of adsorbates, and (iii) clustering by attractive interactions between adsorbates. Unfortunately, these models often fail to explain molecular reactions on semiconductors. Sticking coefficients of chemical species on semiconductor surfaces are often very weak, and chemical species tend to adsorb preferentially at specific atomic sites, with adsorption rates decreasing once these sites have all reacted. In addition, surface diffusion of the adsorbed species is usually insignificant because of the presence of localized surface electronic states that reduce the surface mobility (as compared with metals). It is, therefore, difficult to understand a priori how molecular reactions starting at specific sites on semiconductor surfaces progress to completion across the whole surface.

We have studied how site-specific chemical character influences surface organization for GaAs(111) A and B surfaces (I). Here, the A surface is the one terminating with only Ga atoms, and the B surface is the one terminating with only As atoms. The surface is termed (111) according to a convention that defines the

The author is at the Centre for Advanced Nanotechnology, University of Toronto, Toronto, Ontario, Canada M5S 3E4. E-mail: ruda@edf.utoronto.ca

exposed surface in terms of the plane of the underlying bulk structure it exposes. The propagation of lateral interactions results from the fundamental inability of Ga-terminated surfaces to match the underlying As layers and As-terminated surfaces to match the underlying Ga layers. This results in a cumulative lateral force, which is sufficiently strong to eject atoms at specific periodic locations. The surface then relaxes into its final organization. This so-called reconstructed surface exposes different configurations of active atomic sites than would the unreconstructed bulk termination, affecting the interaction of the surface with other chemical species. Identifying the exact surface structure is thus a prerequisite for understanding the interactions of such surfaces with foreign species.

One of the most important processes in semiconductor technology is epitaxial growth, in which an underlying substrate determines the structure of another material grown on top of the former. The reaction of chemical species responsible for this process on GaAs(001) has been studied by Avery and co-workers, who used STM to examine submonolayer island size distributions to infer the nucleation and growth kinetics of islands (2). The basic processes controlling island kinetics are adatom mobility, adatom interactions during island formation, and interactions between adatoms and step edges that are responsible for island growth (3).

In a recent STM study, Liu and coworkers examined the site selectivity of the reaction of bromine, Br₂, with GaAs(001) surfaces (4). They found that the Br_2 molecules only reacted with second-layer Ga atoms on the As-rich GaAs(001) surfaces (see figure). As the Br₂ molecule approaches the surface, the highest occupied molecular orbital (HOMO) of the Br₂ molecule interacts with an empty Ga-dangling bond, generating a net attraction that steers the incident molecule toward a Ga atom. In contrast, the interaction of the HOMO of Br_2 with the filled dangling bond of a top-layer As-As dimer is repulsive and acts as a shield for the strained As-As dimer bonds and As-Ga back bonds in the top layer. Similar arguments have been used to explain the observation that center Si atom-dangling bonds are more reactive to F₂, Cl₂, and Br₂ than corner Si atom-dangling bonds on Si(111) surfaces; the former are less filled than the latter (4). In support of this interpretation, Cho and co-workers recently showed that during adsorption and desorption of hydrogen on Si(111) surfaces, localized dangling bonds bend toward an incoming hydrogen molecule to facilitate its dissociation (6).

SCIENCE'S COMPASS

Surface response and charge exchange between chemical species and semiconductor surfaces are important in the interactions of oxygen and sulfur with GaAs(001) surfaces (7, 8). Oxygen atoms first adsorb in a near bridge-bonded formation, causing Ga dimers to be released from the surface; this only partially alleviates the surface lattice distortion caused by the reconstruction. As a result, the oxygen HOMO is pushed below and the lowest unoccupied molecular orbital defined excitation source of atomic dimensions, enabling investigation of local and nonlocal effects. Stipe and co-workers found dramatically different behavior for the different atoms that make up the Si(111) unit cell under electron tunneling. Experiments such as these underline the need to consider the spatially resolved electronic properties responsible for the interactions, stability, and dynamics of chemical species on semiconductor surfaces.



GaBr in trench GaBr at As-As atomic vacancy

Close encounters on a surface. (A) STM image of the reconstructed GaAs(001) surface after reaction with bromine. (B) Schematic illustration of the bonding between bromine and Ga or As on the surface.

(LUMO) is pushed above the GaAs bulk energy band gap. The surface states, which initially lay within the bulk band gap, are therefore moved out of the gap as a result of the oxygen adsorption process. Moreover, each oxygen atom retains a charge of -0.5 e in its final site, nearly embedded in the surface. In contrast, reaction with sulfur results in the Ga surface dimers becoming fully opened, hereby permitting surface Ga atoms to assume a near ideal surface arrangement. closely resembling the unreconstructed bulk termination. The bridge-bonded S atoms retain a charge of -0.6 e. As a result, the sulfur HOMO is lowered and the sulfur LUMO is raised compared with the GaAs bulk bandgap edges; however, the HOMO states are still above the valance band edge, leaving the gap still containing surface states. The charge distribution and surface electronic states resulting from these reaction processes directly influence the continued reactivity of such surfaces to these and other species.

Insights into how electrons interact with such surfaces can also help in understanding surface reactivity. Stipe and co-workers have reported on the reversible lateral displacement of specific Si adatoms on a bare Si(111) surface under the influence of tunneling electrons (9). When current flows between an STM tip and the surface, the potential of the surface adjusts relative to the bulk to support the current; electrons from the STM tip can then provide a wellThe vibrational spectra of single molecules adsorbed on a copper surface recently obtained by this group (10) also promise to provide detailed insights into chemical processes on surfaces.

The examples given above illustrate the power of recently developed experimental STM-based techniques to probe the structural and electronic signatures of phenomena occurring on the atomic scale. Coupled with computer modeling, which can provide increasingly realistic descriptions of the pertinent underlying physics, these studies are providing the information needed to understand and control the interactions of chemical species on semiconductor surfaces. This research will have a profound influence on nanotechnology, slated to become the cornerstone of coming generations of semiconductor devices and circuitry.

References

1.

- J. G. Ping and H. E. Ruda, J. Appl. Phys. 75, 5332 (1994).
- A. R. Avery, H. T. Dobbs, D. M. Holmes, B. A. Joyce, D. D. Vvedensky, Phys. Rev. Lett. 79, 3938 (1997).
- Z.Y. Zhang and M.G. Lagally, Science 276, 377 (1997).
- Y. Liu, A. J. Komrowski, A. C. Kummel, Phys. Rev. Lett. 81, 413 (1997).
- J.A. Jensen, C. Yan, A. C. Kummel, ibid. 76, 1388 (1996). 6. K. Cho, E. Kaxiras, J. D. Joannopoulos, ibid. 79, 5078
- (1997).
- 7. J. G. Ping and H. E. Ruda, J. Appl. Phys. 83, 5880 (1998). , ibid. **79**, 3758 (1996).
- 9. B. C. Stipe, M. A. Rezaei, W. Ho, Phys. Rev. Lett. 79,
- 4397 (1997). _, Science **280**, 1732 (1998). 10.