Defect Engineering in Semiconductors for Nanoelectronic Devices

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Abstract-**Many designs for nanoelectronic devices rely on semiconductor materials, whose properties depend upon point defects. Control of the number and spatial distribution of these defects is becoming increasingly important. Here, principles are outlined for accomplishing such control via manipulation of the chemical state of nearby surfaces and via photostimulation. The key mechanisms have been discovered only recently, and should operate with special effectiveness at the nanoscale.**

I. INTRODUCTION

A significant number of designs for nanoelectronic devices and nanosensors rely on semiconductor materials. Examples include gas sensors made from zinc oxide nanowires and fluorescent markers made from zinc sulfide or cadmium selenide. Key aspects of device performance, such as florescence yield and electrical conductance depend upon the presence of native point defects such as vacancies and interstitial atoms. Yet during the device fabrication process, these defects can be mobile enough to react with nearby surfaces, with those surfaces serving as either sources or sinks. Little attention has been paid to this form of surface chemistry, although it is especially important at the nanoscale where all regions are in close proximity to a surface or interface. Indeed, solid-state diffusion measurements and modeling in our laboratory have shown that reactions between defects and surfaces can play the dominant role in regulating semiconductor defect concentrations, sometimes in a controllable way. Here, methods are discussed for accomplishing such control via manipulation of surface chemical state and via photostimulation. Silicon and titanium dioxide are employed as prototypical materials to demonstrate the principles.

II. SURFACE EFFECTS

We have shown that surfaces and solid-solid interfaces can couple to the semiconductor bulk through electrostatic interaction with charged defects. Many semiconductor surfaces support electrically charged defects that induce near-surface band bending. One effect of the band bending is the creation of a near-surface electric field, which can attract or repel charged bulk defects from the surface. A second, less obvious effect of the band bending is that it can change the charge state of the bulk defects near the surface where the band bending is largest and the position of the Fermi level is most perturbed. In doped semiconductors such as silicon, the change in charge state interacts with the electric field in a way that induces a near-surface pileup of dopant within the first few nanometers of the surface. We have also seen evidence for such a phenomenon in TiO_2 by monitoring diffusion of ^{18}O from the surface into the bulk.

Another mechanism for interaction between defects and surfaces involves insertion of interstitials into dangling bonds at the surface. Surfaces differ markedly in their ability to annihilate defects. For example, adsorption should exert significant effects. An atomically clean surface can annihilate interstitial atoms by simple addition of the interstitials to dangling bonds. However, if the same surface becomes saturated with a strongly bonded adsorbate, annihilation requires the insertion of interstitials into existing bonds. Such insertion should have a higher activation barrier and a correspondingly reduced probability of occurrence. A schematic diagram of this idea appears in Fig. 1. Analogous arguments can be made for creation of bulk defects from a surface. We have shown that silicon surfaces can serve as either sources or sinks of interstitial atoms depending upon circumstances, and we are developing parallel evidence for oxygen in TiO_2. Indeed, we have shown that the surface pathway for creating defects sometimes changes the entire mode of defect-mediated diffusion in the bulk.

For both these mechanisms, modeling of the detailed reaction pathways of defects plays an important role in designing appropriate experiments and interpreting the results.
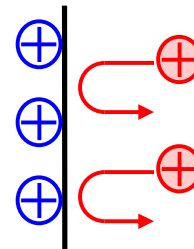

Fig. 1. Interaction of bulk charged defects with charge built up at a surface or interface.

III. PHOTOSTIMULATION EFFECTS

We have shown that the diffusion rates of arsenic and silicon isotopes within silicon are increased nonthermally by more than an order of magnitude by modest optical illumination intensities of ~1 W/cm^2. Photostimulation acts to change the average charge state of the dominant diffusing point defect, which in turn translates into changes in defect mobility, concentration or both. The photostimulation effects extend to other semiconductors including metal oxides, and significant illumination effects on ^{18}O diffusion profiles have recently been observed, as shown in Fig. 2. We also have evidence, that photostimulation may change the average charge state of defect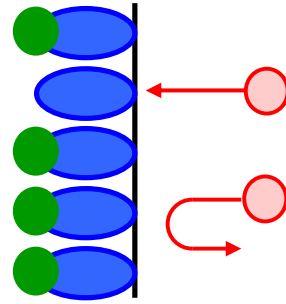s on the surface. This change would then affect the nature of the electrostatic coupling between the charged surface and bulk defects.

Fig. 2. Interaction of bulk defects with dangling bonds at a surface or interface. Saturated bonds tend to "repel" approaching defects.