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Photoinduced formation of dimers at a liquid/(001)GaAs interface

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Using reflectance anisotropy spectroscopy (RAS), we show that surface dimers, which so far have only been observed on surfaces in an ultrahigh-vacuum environment, can exist at semiconductor/liquid interfaces. We consider here As and Ga dimers at the interface between GaAs and sodium sulfide solutions. These dimers appear as the result of photochemical reactions and are identified by their RA signatures. Their observation requires (i) dark treatment of the surface in the solution (1 h) in order to form an overlayer which isolates the surface from the solution, (ii) subsequent above band-gap light excitation which induces photoassisted breaking of respectively As-related and Ga-related chemical bonds at the interface between the semiconductor and the protective layer. Analysis of the growth under light excitation of the dimer signal gives evidence that gallium dimers are created at the expense of arsenic dimers by breaking of chemical bonds between gallium and overlying arsenic atoms. [S0163-1829(96)50636-3]

Surface dimers appear on the (001) GaAs surface during growth processes[1] or due to thermally-assisted breaking of surface bonds under annealing in an ultrahigh-vacuum (UHV).[2] These dimers are the building blocks of the reconstruction of (100) semiconductor surfaces, and have so far been directly observed on well-characterized surfaces in the UHV environment. The most direct technique for observation of these dimers is probably reflectance anisotropy spectroscopy (RAS) (Refs. 3 and 4) which allows one to monitor optical transitions between dimer-related electronic levels through their anisotropic characteristics. Using this last technique it has been shown that surface dimers can be used as a probe for surface chemistry.[5]

The present work is a demonstration of the existence of dimers at a liquid-semiconductor interface, and of their use as a probe for investigating chemical reactions at this interface. We have used GaAs immersed into sodium sulfide solutions, for which (due to chemical reactions which occur at the interface[6]) a sulfide layer is formed between the semiconductor surface and the solution. This layer, which has been shown to improve the surface electronic properties,[5,7] isolates the semiconductor surface from the liquid and allows formation and conservation of dimers at this surface.

We demonstrate that these dimers are created through photoassisted breaking of chemical bonds. Such photochemical reactions have been widely investigated in electrochemical environment,[8] but have never been studied in the case of sulfide passivation of semiconductors. Investigations of the time dependence and of the light excitation energy dependence of the dimer signal allow us to characterize the basic mechanism of these photochemical reactions. These reactions can explain some results on the chemistry of sulfide-passivated GaAs obtained using experimental techniques based on light excitation of above band-gap energy.

RA spectra were taken using a setup described elsewhere.[9] RA spectroscopy measures the relative difference $\Delta R/R=(R_{1\bar{1}0}-R_{110})/R$ of the near-normal reflectivities for light polarized along the $[1\bar{1}0]$ and $[110]$ principal axes of the (001) surface as a function of photon energy. In general, a nonzero RA signal can originate from three main reasons. Well-resolved RA features are caused by surface dimers[4,5] or by the linear electro-optic effect induced by the surface electric field.[10] On the other hand, macroscopically anisotropic overlayers or surface roughness give rise to a very broad structureless spectrum.[11]

For p-type GaAs of doping concentration 10^{18} cm^{-3} and for a 0.6-M Na_2S solution, the results are shown in Fig. 1. Figure 1, curve a shows the RA spectrum obtained immediately after immersion into the solution. This spectrum consists of a broad signal with a derivativelike feature which is known to be induced by the strong surface electric field of our highly doped material. The decrease of the RA signal for energies above 3.8 eV is caused by light absorption in the solution. Curve b in Fig. 1 is the RA spectrum after a delay of 1 h during which the sample was carefully shaded from any light. We have verified that the weak light excitation used for RA measurements has a negligible effect on surface chemistry. The difference between the two spectra is shown in Fig. 1, curve d. Apart from the feature near 3 eV, which reflects the change of the surface band bending in the solution,[9] this spectrum has a broad structureless form.

We explain the appearance of this broad signal as being due to the formation of a surface passivating overlayer. Such a layer, already found by photoemission spectroscopy,[5,12,13] and infrared spectroscopy,[14] contains sulfur and the products of the chemical reactions which occur at the semiconductor-liquid interface. Below 3.2 eV, the difference spectrum (Fig. 1, curve d) is qualitatively accounted for (Fig. 1, curve e) by a model[11] which describes the effect of an anisotropic non-

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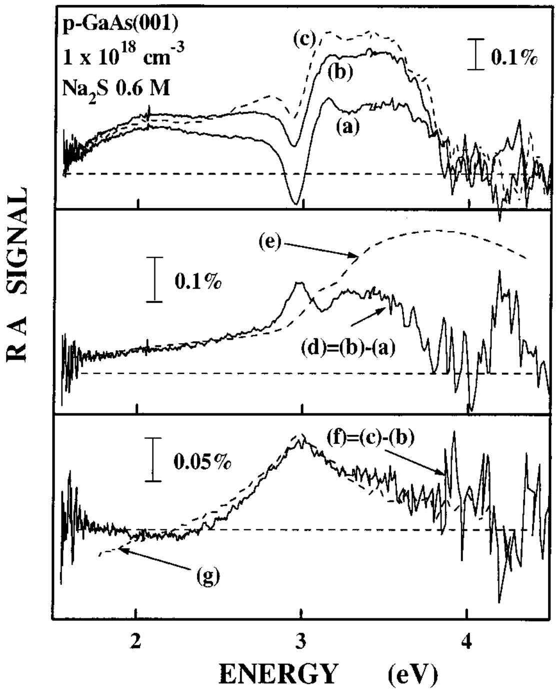

FIG. 1. Variation of the RA spectrum of GaAs due to immersion into 0.6-M sodium sulfide solution. Curve *a* is the spectrum immediately after immersion. Curve *b* is the spectrum after 1 h treatment in darkness. Curve *c* is the spectrum after subsequent excitation by above band-gap light. Differential signals are shown, respectively, in curves *d* and *f*. Curve *e* is the result of a calculation. Curve *g* is the characteristic RA signal of As dimers, obtained in UHV conditions, divided by a factor of 3.

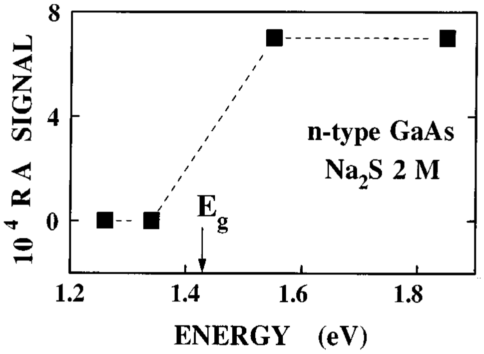

FIG. 2. Dependence of the photoinduced effect on the energy of exciting photons. The dimers are induced only if the light energy is larger than the band gap of GaAs (E_g).

absorbing overlayer or of anisotropic surface roughness. This roughness can be produced by anisotropic etching, and has been found on GaAs to induce similar broad signals.[15] However, the observed RA signal cannot be due to anisotropic etching, since similar RA spectra are found for both *n*- and *p*-type materials, whereas the etching of GaAs in sodium sulfide solutions is observed only for *n*-type material.[16] We have also observed that the broad signals arising after dark treatment are strongly reduced after water rinsing, which is known to remove most of the overlayer.[17]

The growth of the induced RA signal saturates after 1 h in the dark, which indicates that the formed overlayer isolates the semiconductor from the liquid. At this stage, we apply light excitation using a white light source and a high-pass filter for a time of only 3 min ($h\nu > 2$ eV, power density 10 mW/cm^2). In Fig. 1, curve *c* presents the RA spectrum after such illumination. The difference between RA spectra before and after illumination, shown in curve *f*, consists of a positive line which peaks at 3 eV. This line is narrower than the broad spectrum of curve *d*, as its full width at half maximum is of the order of 0.5 eV. This line has the same sign and position as the RAS contribution of arsenic dimers on (001)GaAs.[18]

Assignment of this RA line can be made using a comparison with a spectrum taken in UHV conditions. Figure 1, curve *g* shows the spectrum of an undoped sample passivated in a sodium sulfide solution and annealed in UHV at 450 °C, which was shown to produce the breaking of As-related surface bonds and to induce As dimers.[5,18] This spectrum closely corresponds with the one taken in liquid environment (curve *f*). Such good agreement demonstrates the presence of arsenic dimers underneath the overlayer, formed by photochemical breaking of As-related bonds. The dimer concentrations are of the same order of magnitude, as curve *g* represents the RA signal obtained in UHV conditions divided by a factor of only 3. We estimate that a light excitation dose of the order of 10^5 photons per dimer is necessary for this reaction. We point out that these dimers are very stable, as they can be kept under the protective layer for a duration as long as several hours. For a sodium sulfide solution, this signal is weakly dependent on experimental conditions such as molarity, sample doping, light intensity. The only effect of these parameters is to change the characteristic times for building up of the protective layer (higher molarity leading to shorter times), and for appearance of dimers.

The photochemical breaking of As-related bonds, on the other hand, strongly depends on light energy. This is shown in Fig. 2 which presents the dependence of the dimer signal on photon energy for *n*-type GaAs of doping concentration 10^{18} cm^{-3} and for a 2-M Na$_2$S solution. There is a threshold at the band-gap energy which demonstrates the role of photoexcited carriers in the semiconductor. No As dimers are created for illumination at an energy smaller than the GaAs band gap, and above this band gap the intensity of the arsenic dimer line does not depend on the photon energy. A similar spectral dependence is generally observed for photodesorption of foreign atoms from semiconductor surfaces. In the same way as usually supposed in the latter case,[19] we propose that the photoelectrons are captured by the antibonding orbital of As-related surface bonds lying below the conduction band, which decreases the bond energy and induces the breaking of this bond.

The most natural hypothesis is that the relevant bonds are with sulfur atoms. Indeed, our theoretical analysis[16] indicates that, for the concentrations of sodium sulfide solutions that we use (0.1–2 M), S-As surface bonds in bridge-site configuration should be dominant on the passivated surface. On the other hand it was found[20] that the antibonding state of As-S bond lies within the GaAs energy gap and therefore can

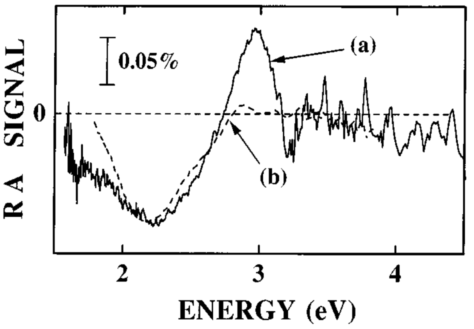

FIG. 3. Curve *a* is the light-induced variation of the RA spectrum for a 1-M Na_2S_x solution. Curve *b* is the characteristic RA signal of Ga dimers, obtained in UHV conditions, divided by a factor of 4.

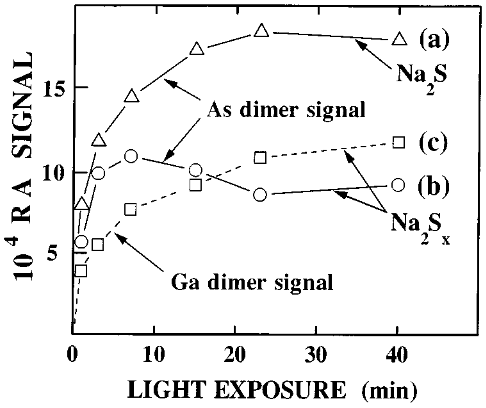

FIG. 4. Effect of the addition of disulfide ions on the dependence of the dimer signals as a function of duration of light irradiation. Curve *a* is the rise of the arsenic dimer signal in a 1-M Na_2S solution. Curve *b* presents the same results for a 1-M Na_2S_x solution. Curve *c* presents, in the same case, the rise of the gallium dimer signal.

be easily occupied by photoelectrons. As a result, these As-S bonds can be easily broken under light irradiation, producing As dimers and an overlayer of physisorbed sulfur. Other possible As-related surface bonds such as As-O and As-As are less reasonable candidates, since no photodesorption of arsenic and oxygen is known for As-capped or oxidized GaAs surfaces.

We have found that, if an additional concentration of sulfur is dissolved into the solution, light excitation also induces gallium dimers at the semiconductor surface. In the following, this sulfur-enriched solution will be called Na_2S_x, where the average sulfur concentration x is of the order of 1.3. Figure 3 presents the results for the same p-type sample in a 1-M sodium sulfide solution. This addition creates disulfide ions, the effect of which is to create a protective layer of increased thickness.[21] The shape of the dark-treatment-induced RA signal, not shown in the figure, is the same as in the preceding case. The light-induced RA spectrum (Fig. 3, curve *a*) also shows, together with the As dimer line, the negative line at 2.2 eV characteristic of gallium-rich surfaces.[5,18] This last line is similar to that found in UHV for an undoped, As-capped sample after an annealing at 550 °C which is known to reveal the gallium-rich surface reconstruction (Fig. 3, curve *b*).[18] Therefore we conclude that the negative RA line of curve *a* is due to gallium dimers.

The mechanism of appearance of gallium dimers is different from the one for arsenic dimers. It cannot be satisfactorily explained by the breaking of Ga-S bonds, because these bonds are very stable,[22] and the antibonding orbital of the Ga-S bond is predicted to lie much higher than the bottom of the conduction band,[20] and therefore cannot trap photoexcited electrons. A study as a function of duration of light exposure confirms that the two mechanisms are different. We used an attenuated light excitation of 10^{-1} mW/cm^{-2} power density in order to follow the change of dimer concentrations. Curve *a* in Fig. 4 shows, as a reference, the rise of the As dimer line for a 1-M Na_2S solution, which does not induce gallium dimers. One observes a monotonic increase with a characteristic time of approximately 10 min. Curves *b* and *c* in Fig. 4, respectively, show the time dependence of the amplitudes of As and Ga dimer signals in a 1-M Na_2S_x solution. In sharp contrast with Fig. 4, curve *a*, the appearance of gallium dimers is correlated with a decrease of the As dimer signal. For a time larger than 10 min, the lacking As dimer signal that is, the difference between curves *a* and *b* is approximately proportional to the arising gallium dimer signal. Using an estimate of the ratio of the oscillator strengths for the two dimers,[18] we find that within an uncertainty of 20%, the disappearance of As dimers produces the appearance of an essentially equal amount of gallium dimers.

These results demonstrate that gallium dimers are formed at the expense of photochemically formed As dimers. The most reasonable explanation is photodissociation of GaAs under the overlayer, which liberates arsenic, uncovers underlying gallium, and therefore induces gallium dimers. Photobreaking of surface Ga-As chemical bonds is known to be initiated by trapping of photocreated holes.[8] Due to the resulting weakening of these Ga-As chemical bonds, it becomes energetically favorable to break this bond and to form a new chemical bond between As and overlying atoms. More detailed chemical analysis will be performed elsewhere.[6]

In summary, we have obtained two main results. First, we have observed gallium and arsenic surface dimers at a semiconductor surface in a liquid environment. The use of these dimer signals as a probe opens new perspectives for investigating surface chemistry of semiconductor-liquid interfaces. Second, we demonstrate the effect of photobreaking of surface chemical bonds. This photosensitivity of As-S bonds at passivated semiconductor surfaces may explain that these bonds have only been observed in the overlayer and not on the semiconductor surface itself, even for adsorption of sulfur on the clean As-reconstructed surface.[2,5]

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