Influence of Heterointerface Atomic Structure and Defects on Second-Harmonic Generation

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Second-harmonic spectroscopy is shown to be sensitive to interfacial electronic traps, lattice relaxation, and buried surface reconstruction in ZnSe/GaAs(001) heterostructures. Newly developed photomodulation–second-harmonic-generation experiments reveal that the interfacial region contains predominantly hole traps, and that the density of these traps is substantially lower for 3 × 1 buried surface reconstructed samples.

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Perfect heterojunctions are difficult to achieve. Dislocations, point defects, and charge traps are a few examples of macroscopic imperfections that arise near the junction. In many cases these structural imperfections play a prominent role in affecting the electronic properties of the entire material. Clearly an important challenge in this field is to identify imperfections, understand their origin, and develop more complete microscopic models of their action.

In this work three-wave-mixing spectroscopy was used to probe interfacial defects and atomic structures in epitaxial ZnSe/GaAs(001) heterostructures. This system has received intense interest recently because laser action has been achieved in ZnSe [1]. The system exhibits a rich phenomenology brought about by an interplay of physics, chemistry, and materials science at the interface. For example, thin ZnSe layers grow pseudomorphically on GaAs and then abruptly relax, leaving dislocations and point defects at the buried interface [2–5]; different reconstructions of the buried GaAs surface created during epitaxial growth induce dramatically different photoconductivity properties [2], and, although charge traps are believed to exist at the interface, their nature and origin are only partially understood [6].

Recently, a robust interfacial excitation has been observed in ZnSe/GaAs(001) heterojunctions by second-harmonic generation (SHG) [7]. The SH spectral feature at 2.72 eV was produced as a result of a virtual coupling between the ZnSe valence band and a *resonance state* of a quantum well located *across* the junction in the GaAs conduction band (see inset in Fig. 1). The interfacial quantum well was brought about by interdiffusion of Zn into GaAs and Ga into ZnSe during sample growth [8].

We have found that this interfacial SH resonance is sensitive to a variety of *structural* phenomena. In essence *any process* that modifies the band profile *near* the junction will affect the strength of the resonance. We have observed the variation of interface SH spectra with respect to lattice strain relaxation and to surface reconstruction of the buried GaAs. In addition, using a photomodulation-SHG (PSHG) technique, we have exploited this sensitivity to determine the nature and relative density of interface charge traps as a function of substrate surface reconstruction. Our results provide new examples of how interfacial crystal structure and band profiles influence three-wave mixing. While second-order nonlinear spectroscopies have been successfully used to distinguish surface structures [9], few SHG experiments

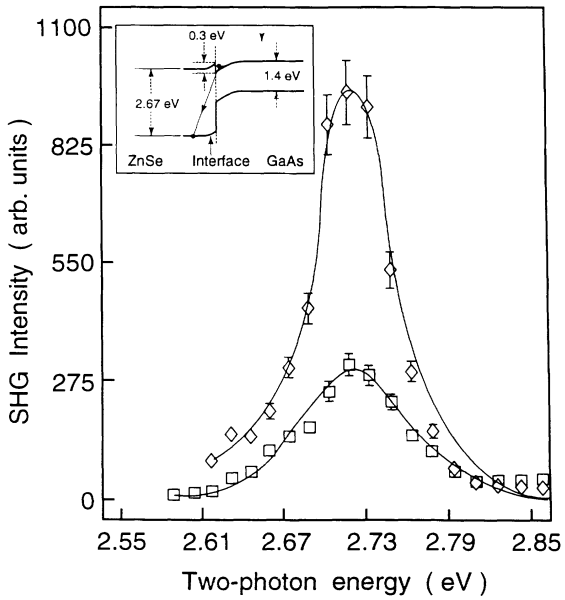

FIG. 1. SHG spectra for 3 × 1 (◇) and 2 × 4 (□) buried GaAs surface reconstructed samples as a function of upconverted photon energy. The 3 × 1 sample exhibits a 4 times stronger peak nonlinearity than the 2 × 4 sample. The ZnSe overlayer thickness was 215 Å for both samples. Solid lines are only a guide for the eye. Inset: Energy-band profile as a function of the depth for the ZnSe/GaAs(001) system. A transition between the quantum well state and the valence band of ZnSe is indicated.

have been performed on buried solid interfaces [7, 10–13]. The present measurements are the first to demonstrate sensitivity to *defect structures at a buried interface.* The success of these experiments suggests that this technique has the potential to be a useful probe of the junction during growth.

Our samples consist of an epitaxial layer of undoped ZnSe(001) grown, in a dual chamber molecular beam epitaxy system [14], on a 0.5 μm undoped GaAs(001) epitaxial film terminated with 2×4 or 3×1 surface reconstructions. The 3×1 GaAs(001) surface reconstructed film has an approximately equal number of Ga and As atoms, and the 2×4 surface reconstructed layer was prepared to have a higher (~75%) concentration of As [2]. The different GaAs(001) surface reconstructions were monitored by reflection high energy electron diffraction (RHEED) during growth. When the desired reconstruction pattern was observed, samples were cooled and epitaxial growth of ZnSe was initiated in an As-free environment [2]. The thickness of the ZnSe overlayer in the 3×1 (2×4) reconstructed sample was 215 Å (~200 to ~5000 Å). These thicknesses were determined by calibrated dosing and by linear reflectivity. The wide range of thicknesses enabled us to study the effect of lattice relaxation on SHG spectra. The SHG measurements were conducted in air using a standard optical apparatus [15].

We first discuss the thickness-dependent measurements on the 2×4 surface reconstructed samples. Although the lattice mismatch in this system is small (0.27% [16]), a thin ZnSe/GaAs(100) heterostructure suffers internal strains. Typically the lattice strain relaxes when the overlayer thickness becomes greater than some critical value. This relaxation is accompanied by the production of misfit dislocations at the interface along with various point defects such as vacancies and interstitials [17]. The SHG spectra for different overlayer thicknesses is shown in Fig. 2. Our data show a marked change as the thickness is increased through the critical regime. All samples with a thickness less than 1330 Å exhibited a peak at 2.72 eV; within our resolution no spectral shift was observed. For samples thicker than 1330 Å, the intensity of this feature dropped dramatically, and the intensity at 2.67 eV is relatively enhanced. In Fig. 2 we plot the normalized peak intensity as a function of thickness. A transition between 1330 and 2000 Å is evident.

These observations are understood in the following context. Misfit dislocations are produced at the buried interface as a result of an abrupt strain relaxation. The line defects are typically surrounded by a space-charge region in semiconductors [18, 19]. We expect line charges at the interface to modify the interfacial electric field such that the band bending on the ZnSe side of the heterointerface is substantially changed, and the resonance state is diminished. Since the SH resonance at 2.72 eV results from a virtual coupling between a resonance state of the quantum well and the valence band of the ZnSe, a substantial change in band bending leads to a marked reduction of the 2.72 eV SHG signal. Our thickness-dependent data demonstrate that the lattice relaxation occurs when the overlayer thickness is greater than 1330 Å (Fig. 2). This is in agreement with previous measurements of the critical thickness utilizing x-ray diffraction [3], photoluminescence, and transmission electron microscopy [4].

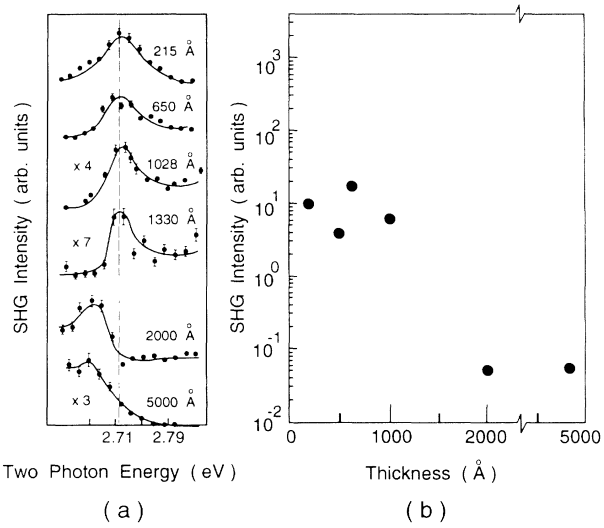

FIG. 2. (a) Interfacial resonance SHG spectra near 2.72 eV, as a function of overlayer thickness. The critical thickness is between 1330 and 2000 Å. Note that the resonance vanishes over this thickness range, and the vertical scale is linear. (b) Normalized SHG peak intensity at 2.72 eV as a function of overlayer thickness. The data, derived from (a), exhibit a dramatic drop for overlayers thicker than 1330 Å.

We next turn our attention to interfacial defects in the *pseudomorphic layers*, whose number density depends on the surface reconstruction of the buried GaAs. Generally the electronic distribution around these defect centers leads to the creation of metastable electronic states within the gap [18, 19]. These metastable electronic states have the propensity to trap free carriers, and thereby also modify the interface electric field and band profile. The SHG feature at 2.72 eV is affected by changes in interface band profiles, and our PSHG experiments reveal more information about these phenomena.

In the PSHG experiments we have measured the intensity of the 2.72 eV SH resonance as a function of the fluence and wavelength of a photoexciting light source [7]. The sample was illuminated at normal incidence by light from a tungsten lamp monochromator or an argon-ion laser, *while the SHG experiment was in progress.* The intensity of the photoexciting beam was monitored simultaneously, and never exceeded 0.5 mW/cm^2. Typically the sample was illuminated for a period of ~2 min to ensure steady-state conditions were reached.

We have made two important observations about the effect of substrate surface reconstruction on the SHG sig-

nals. The first concerns the variation of the SH resonance intensity as a function of lamp intensity derived for both reconstructed samples in separate PSHG experiments (Fig. 3). With a blue (3 eV) photoexciting light source, the 3×1 reconstructed sample required more photogenerated carriers than the 2×4 reconstructed sample to achieve the same fractional SHG signal reduction. The results of the second observation are shown in Fig. 1. Here the SHG spectra of two samples with the same overlayer thickness but different surface reconstruction of the substrate are compared. One can readily see that the sample with 3×1 reconstruction exhibits a much stronger peak than the 2×4 sample.

In the PSHG experiment, photoexcited carriers are separated by a strong interfacial electric field (see Fig. 3). Some of these carriers will be trapped by charged interfacial defects near the junction, and will change the total interfacial charge. The new interface charge will modify the band bending, and perturb the states associated with the quantum well. Interfacial trapped holes *decrease* the interface negative charge and decrease (increase) the band bending on the ZnSe (GaAs) side of the junction. This delocalizes the quantum well wave function and reduces its relative amplitude within the well. As a result a drop in the SHG signal is expected. Alternatively, interfacial trapped electrons will *increase* the SHG signal. Related band bending effects from externally applied bias voltages have also been observed by electrolyte electroreflectance [20]. We observed a drop (increase) in SH intensity when the sample was illuminated with 3.0 (2.4) eV lamp photons. The 3.0 (2.4) eV photons produce holes (electrons) in ZnSe (GaAs) that migrate in the junction field toward the interface where they can be trapped. Our observation that the 3×1 reconstructed sample required more blue photons than the 2×4 sample to produce the same effect suggests, in agreement with model calculations [21], that the 3×1 reconstructed sample has a lower hole trap density. Note also that these phenomena cannot be explained by the optical pumping of electrons into the quantum well resonance state [22].

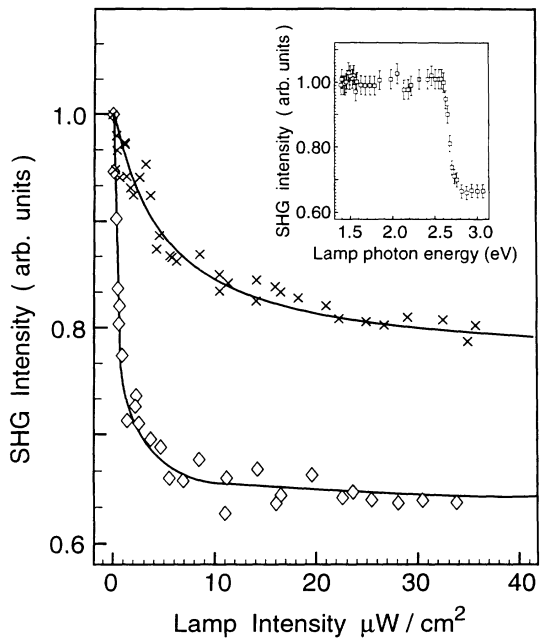

FIG. 3. Fractional change of the interfacial resonance SHG peak intensity at 2.72 eV for 3×1 (×) and 2×4 (◇) samples as a function of lamp intensity using lamp photons with an energy of 3.0 eV. The solid lines are the best fit to the data. The SHG intensity reached its saturation level at ~10 μW/cm^2 for the 2×4 sample. The saturation condition was not achieved for the 3×1 sample in our lamp intensity range. Inset: Variation of the resonance interface SHG peak intensity at 2.72 eV as a function of lamp photon energy. The intensity transmitted into the sample was kept constant at 10 μW/cm^2.

A detailed analysis [23] of the data in Fig. 3, along with additional trap lifetime experiments [24], have enabled us to make a stronger and more precise statement about the relative hole trap densities. Briefly, we find that

$$(k\alpha N)_{2\times4\text{ sample}}/(k\alpha N)_{3\times1\text{ sample}} \simeq 10,$$

where N is the density of interfacial hole trap centers and k is the rate constant at which an unoccupied trap center will trap a hole at the interface. The parameter α represents the deviation of interfacial free hole density from its thermal equilibrium value per unit of lamp light intensity. Intuitively we expect α to be bigger in systems with a lower number of trap and scattering centers. Our time-dependent measurements [24] indicate that k is about the same in both samples. Thus we can argue that the trap density in the 3×1 sample is *at least* 10 times less than in the 2×4 sample. A similar analysis on PSHG data, with 2.4 eV carrier generating photon, indicates that the electron trap density in the 3×1 sample is *at least* 3 times less than in the 2×4 sample. The lower trap densities should also be expected to enhance the size of the 3×1 SH resonance with respect to the 2×4 resonance (Fig. 1), in analogy with photoconductivity measurements on these systems [2], where the 3×1 reconstruction exhibits a factor of ~50 increase in photocurrent over the 2×4 system.

The last conclusion of the PSHG work is derived from the data in the inset of Fig. 3. Here we examine the SH intensity as a function of lamp photon energy in the 2×4 sample. The lamp intensity transmitted into the sample is held constant at 10 μW/cm^2. Although the efficiency of carrier generation in GaAs is much greater than in ZnSe [25], we see no effect as a result of carriers in GaAs at this intensity level. Since electrons in GaAs and holes in ZnSe both move toward the interface, these observations suggest that the interface traps are mainly *hole* traps, and that the 2×4 interface is *negatively* charged initially. This result is consistent with the prediction of

negatively charged bonds at the interface [21].

In conclusion, we have utilized second-harmonic spectroscopies to study lattice relaxation, substrate surface reconstruction, and interfacial defects in ZnSe/GaAs(001) heterostructures. We have demonstrated the sensitivity of the SH probe to lattice relaxation and critical thickness in this system. Our measurements also suggest that the interface trap centers are primarily hole traps, and that the 3×1 buried GaAs surface reconstruction introduces fewer interface traps.

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[22] Our PSHG data as a function of lamp photon energy, depicted in inset of Fig. 3, exhibit that the maximum rate of change of the SHG intensity is at the ZnSe optical band gap energy of 2.67 eV and not at 2.72 eV. This fact along with the observed *increased* SHG intensity as a result of 2.4 eV carrier exciting photons does not support the optical pumping mechanism.

[23] In our analysis we modeled the number density of holes trapped at the interface by a localized rate equation. The steady-state solution depends on the number of free holes at the interface that are provided by lamp photons. In our treatment we assume that the density of free carriers at the interface depends linearly on the intensity of the lamp light. The validity of this linear approximation was confirmed experimentally in Ref. [24]. Our data in Fig. 3 were thus fitted by the steady-state solution in order to obtain the best value of $k\alpha N$.

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