Interface Quantum Well States Observed by Three-Wave Mixing in ZnSe/GaAs Heterostructures

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Three-wave mixing was used to spectroscopically probe the interface electronic structure of a buried ZnSe/GaAs(001) heterointerface from 1.3 to 4.3 eV. An unusual resonance at 2.72 eV was observed and assigned to a virtual transition between the valence band of ZnSe and a quantum well state at the buried heterointerface. This assignment was confirmed by experiments that combine three-wave mixing with photoinduced band bending. The experiments also indicate the resonance may be a useful probe of defects at the buried interface.

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When two crystalline semiconductors are abruptly adjoined, an interfacial region is formed whose physical properties are fundamentally different from those of the neighboring bulk materials. Since the microscopic characteristics of the junction determine the macroscopic properties of the material, it is desirable to identify energy states that arise in the region. Unfortunately the buried solid interface is difficult to study experimentally. Although new methods have been developed and used with limited success to reveal specific features about the buried interface [1], the basic problem remains: traditional optical spectroscopies lack interface specificity, and traditional surface diagnostics have a limited penetration depth.

Three-wave-mixing (3WM) spectroscopy is an exciting and relatively unexplored probe of buried solid interfaces [2–5]. It possesses long penetration depths characteristic of most optical methods, and intrinsic interface specificity characteristic of second-order optical processes. The first and only demonstration of 3WM as a *frequency-dependent* probe of buried solid interfaces was carried out recently on the CaF_2/Si interface [3]. These experiments exhibited an interface band gap that was understood to arise microscopically as a result of new bonding and antibonding states between Ca and Si atoms at the junction. Despite this auspicious beginning, we have barely begun to develop a microscopic understanding of the role played by *interfacial excitations in affecting nonlinear optical phenomena.* These processes are of fundamental interest in their own right, and their elucidation should accelerate the development of 3WM as a probe of these systems.

In this Letter we present frequency domain measurements of the ZnSe/GaAs(001) heterojunction by second-harmonic (SH) and sum-frequency (SF) generation. Our experiments reveal an unusual three-wave-mixing resonance that arises as a result of virtual transitions between an interfacial quantum well state and the ZnSe valence band. The observation introduces a new class of nonlinear optical phenomena at interfaces that can provide useful information about band profiles, diffusion, and defects along the boundary of two semiconductors. The observed resonance is shifted to the blue with respect to the bulk E_0 transition in ZnSe, and has been measured in samples with different overlayer thicknesses and interfacial reconstructions. The new resonance is surprisingly strong in comparison to *dipole allowed* bulk transitions, and is also extremely sensitive to band bending induced by weak photoexcitation. The wavelength and intensity dependence of these variations will be discussed, and compared to those of other bulk and interface features.

The ZnSe/GaAs heterostructure was chosen in part because it has been carefully studied morphologically, chemically, and electrically [6]. Research on the heterostructure has been driven primarily by potential optoelectronic applications of ZnSe in the blue spectral region [7]. Our samples were all pseudomorphic heterostructures consisting of an epitaxial layer of undoped ($n \leq 1 \times 10^{15}$ cm^{-3}) ZnSe(001), grown on an 0.5 μm undoped ($n \leq 5 \times 10^{15}$ cm^{-3}) GaAs(001) film terminated with a 2×4 surface reconstruction. The thickness of the ZnSe films ranged from 50 to 1400 Å. The entire heterostructure was grown on an n^+ silicon-doped GaAs substrate in a dual molecular-beam epitaxy chamber [8].

The SHG spectra for each sample were obtained by irradiating the structure with light from a Q-switched Nd-YAG pumped tunable dye laser at an incidence angle of 75°. The incident light pulses had a temporal duration of 9 nsec, and a fluence of ~5 mJ/cm^2. The reflected SH power was measured as a function of dye laser wavelength, and normalized using a quartz plate reference.

ZnSe and GaAs are zinc-blende crystal structures and therefore lack inversion symmetry. Both crystals have a single nonzero bulk second-order susceptibility, $\chi^{(2)}_{xyz}$, whose contribution to the output radiation is highly

anisotropic. We separated the bulk and the interface contributions by proper choice of sample orientation and light polarization [9]. In the p-in/s-out polarization configuration the bulk SH power is proportional to $\cos^2(2\phi)$, where ϕ is the angle between the crystalline [100] direction and the plane of incidence. By setting $\phi = 0$ and employing the p-in/p-out polarization configuration we were able to suppress the bulk $\chi^{(2)}_{xyz}$ signal by $\geq 10^4$, and thereby greatly enhance our sensitivity to interface features. Results obtained in the p-in/p-out (p-in/s-out) configuration with $\phi = 0$ will hereafter be referred to as interface (bulk) signals.

The interface and bulk SH spectra for a sample with 215 Å ZnSe overlayer thickness are shown in Fig. 1. The interface spectra exhibit sharp peaks at 2.92 and 2.72 eV. Separate sum-frequency experiments confirmed that these are *two-photon resonances* (i.e., the features are resonant with upconverted photons). The bulk SH *intensity* exhibits no apparent resonances around 2.72 eV. In order to understand these exciting spectral differences, we carried out a series of overlayer-thickness-dependent studies on the bulk features [10]. Analysis of these measurements yielded the frequency dependence of $\chi^{(2)}_{xyz}$ in ZnSe. The deduced $\chi^{(2)}_{xyz}$ is shown along with the interface SH intensity data in the inset of Fig. 1. The bulk resonance at 2.67 eV corresponds to the E_0 transition in ZnSe. Its

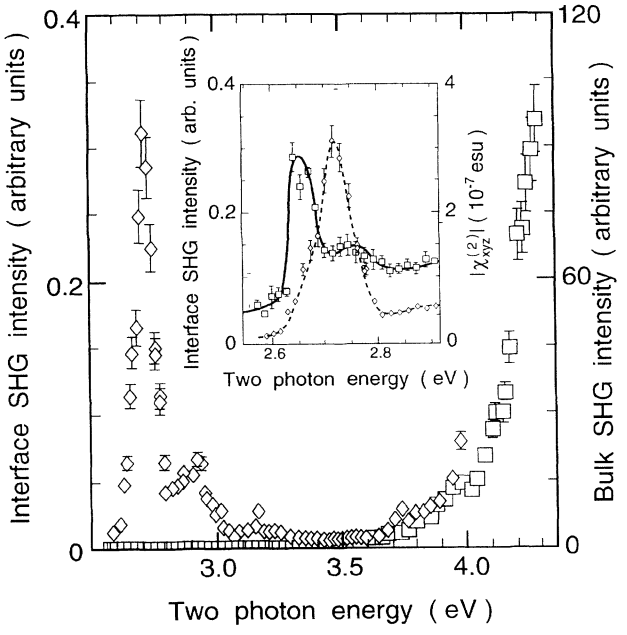

FIG. 1. Normalized SHG intensity of the interface (◇) and the bulk (□) of ZnSe/GaAs(001) as a function of upconverted photon energy; the ZnSe overlayer thickness was 215 Å. Inset: The deduced $\chi^{(2)}_{xyz}$ of the bulk of ZnSe overlayer (□) is compared with interface SH spectra (◇). Solid lines are only a guide for the eye.

shift of 50 meV with respect to the interface feature is $\sim 4\times$ too large to be attributed to the measured strain in the system [11], and offers a first indication that the interface resonance is not purely a bulk effect.

The interface signals can in principle contain contributions from the front surface, and higher-order bulk nonlinearities. It was not possible to measure these contributions using thick (≥ 2 μm) ZnSe samples because they exceed the critical thickness (~1500 Å) and are no longer pseudomorphic. Therefore we undertook different experiments to investigate these effects. We first modified the front surface by chemical etching and by sputtering. Auger electron spectroscopy and scanning electron microscopy revealed that the first 50 Å of the etched ZnSe overlayer was roughened and chemically modified. No change in SH spectra was observed however. Similarly UHV Ar^+ sputtering of a few monolayers near the ZnSe surface did not induce quantitative changes in the spectrum. In another vein we measured the overlayer thickness dependence of the reflected SHG as a function of photon energy. The variation of the SHG intensity with respect to overlayer thickness depends quantitatively on the spatial origin of the signal. For example, the variation of the interface feature at 2.92 eV was well described by a model whereby the ZnSe overlayer attenuates a signal produced *below* the interface. The energy of this feature is consistent with the E_1 transition of GaAs, and we have tentatively assigned this feature to these transitions in the buried GaAs. On the other hand, the *bulk* SH intensity oscillated as the overlayer thickness was increased. This behavior is expected to arise when the material nonlinearity is constant throughout the overlayer [10]. The behavior of the interface feature at 2.72 eV differed substantially from both limiting cases above. The possibility of higher-order bulk contributions were also examined in the s-in/s-out and s-in/p-out polarization configurations. The bulk anisotropic contribution (ξ) was below our noise level and the signal resulting from linear combinations of γ and $\chi^{(2)}_{\|\|\perp}$ was 2 orders of magnitude smaller than interface signal. In total, the evidence indicated that the 2.72-eV feature was influenced by the buried interface and that the ZnSe overlayer also affected the phenomena.

These and other experimental inconsistencies led us toward a new picture of this effect. It is known that Zn and Ga diffuse across the buried interface during the growth [12]. The diffusion length for Ga (Zn) in ZnSe (GaAs) is about 30 Å (100 Å) so that relatively high (4×10^{19} cm^{-3}) dopant densities arise near the interface [13]. Because Zn is an acceptor in GaAs and Ga is a donor in ZnSe, their diffusion produces an intrinsic band bending at the interface (see Fig 2). As a result of this band bending an interfacial quantum well forms in the GaAs conduction band. Quantum wells at heterointerfaces have been produced and studied in other systems [14]. The ZnSe/GaAs heterojunction differs from most

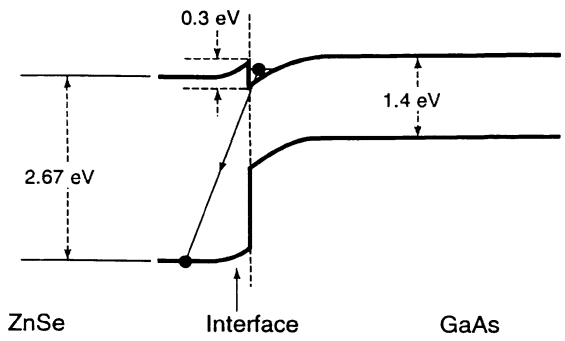

FIG. 2. Energy-band profile as a function of the depth for the ZnSe/GaAs(001) system. This band profile has been determined by solving the Poisson's equation for a Gaussian charge distribution with parameters given in Ref. [13]. A possible pathway for the transition between quantum well state and the valence band of ZnSe is indicated. The calculated excited-state wave function has some amplitude in the well, and in the ZnSe, but decays quickly in the GaAs.

previous observations because the donors and the acceptors are *generated during growth by interdiffusion* across the junction. In our system a resonant electronic state with energy higher than the conduction band of ZnSe exists in the quantum well. An attractive explanation for the resonance thus presents itself. The SHG feature at 2.72 eV corresponds to a virtual crossover transition between the interfacial quantum well state and the ZnSe valence band. A crossover excitation [15] is a transition between two states whose density of states (DOS) is provided by two spatially *separated* materials. This kind of transition can arise when the wave functions of the terminal states extend beyond the interface. Then the states can be directly coupled by photoexcitation. Ultrasensitive electrolyte electroreflectance (EER) measurements in doped ZnSe/GaAs systems have independently revealed the existence of a crossover transition [13] which was always blueshifted by 40–60 meV with respect to the ZnSe E_0 transition. *To our knowledge this is the first time a crossover transition has been observed to influence the nonlinear optical properties of a material system.*

Within the dipole approximation, 3WM processes involve three electronic transitions (real or virtual) in the media. Since the observed feature is resonant with the upconverted (output) photon, the effect of the *input* field is to transfer an electron (virtually) from the ZnSe valence band to the quantum well state. This excitation process can take place via several different pathways, but the resonant final step of the 3WM process involves some charge transfer across the interface. In contrast to the EER measurements, the crossover SH resonance is a virtual transition, has nearly zero background, and possesses a nonlinearity that is comparable in magnitude to the bulk $\chi^{(2)}_{xyz}$. We speculate that because the virtual transition is accompanied by a substantial charge transfer *across* the interface, a large permanent dipole moment in the intermediate state can arise and enhance the second-order nonlinearity. Regardless of its origin, the strong nonlinearity enables us to conduct more detailed experiments on the phenomena.

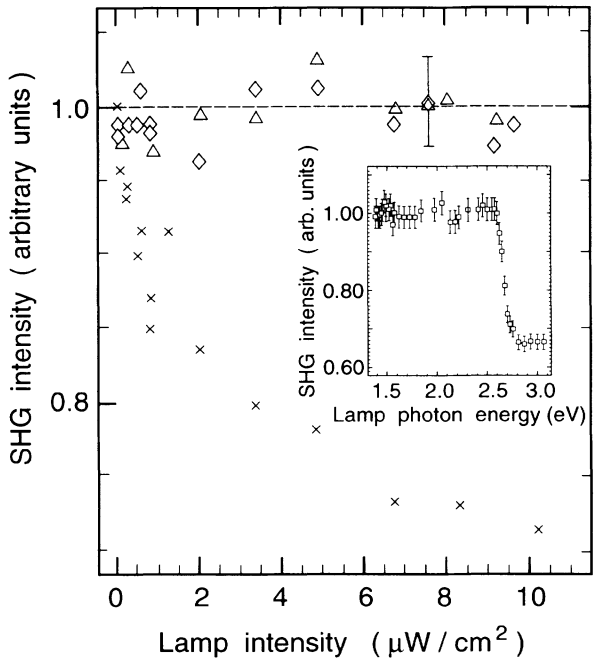

FIG. 3. Normalized variation of the SHG intensity for the interface at 2.72 eV (×) and 2.92 eV (△) and the bulk at 2.67 eV (◇) as a function of the lamp intensity transmitted into the sample at a fixed lamp photon energy of 3.0 eV. Inset: Normalized variation of the resonance interface SHG intensity at 2.72 eV as a function of lamp photon energy. Here the transmitted lamp intensity into the sample is fixed at 10 μW/cm^2. The sample used in these measurements had a 215 Å ZnSe overlayer. Qualitatively similar results were obtained for all other pseudomorphic samples.

Since the quantum well state is produced via band bending and strong built-in fields at the heterointerface, any perturbation of the band bending should affect the interface SH resonance signal at 2.72 eV. We can accomplish this by weakly photoexciting carriers in the sample. In our experiments the sample was illuminated at normal incidence by light from a tungsten-lamp–monochromator, *while the SHG experiment was in progress.* In Fig. 3 we observe the variation of the interface and bulk signals as a function of lamp intensity using a fixed lamp photon energy of 3.0 eV. The bulk and the 2.92-eV interface resonance changed by less than 3% even at the highest lamp powers. In contrast, the 2.72-eV interface resonance exhibits a marked decrease at very low lamp powers. The variation of the intensity of the SH resonance as a function of lamp photon energy is shown in the inset of Fig. 3. In this measurement the lamp intensity transmitted into the sample was held con-

stant at 10 $\mu W/cm^2$. The data exhibit a sharp change in intensity at the band gap of ZnSe. The effects of photoexcited carriers in GaAs were observed at much higher intensities ($\times 100$) by weak laser excitation. These results suggest that carriers produced in both ZnSe and GaAs modify the interface band bending.

Qualitatively we expect photogenerated carriers near the interface to separate in a manner that reduces the built-in field and the band bending [16]. The strength of the induced field is related to the density of the interface defect states (traps) and their lifetimes. Changes in interface band bending of 10% are produced with lamp powers of 1 $\mu W/cm^2$ provided the trapped carrier lifetime is ≥ 1 msec [17]. The weak photoexcitation was observed to cause a reduction in peak SH intensity, but was too small to create a measurable energy shift within our experimental resolution. These observations are consistent with theoretical modeling we have done by integrating the one-dimensional Schrödinger equation for the quantum well potential shown in Fig. 2.

The photoexcitation-SHG measurements thus lead us to conclude that the two interface resonances at 2.72 and 2.92 eV are intrinsically different. This corroborates our earlier assignment of the 2.92-eV resonance to the E_1 transition of buried GaAs. *The photoexcitation was not observed to significantly affect any bulk signal.* In the present context the photoexcitation-SHG measurement depends on band bending at the interface and is highly sensitive to the density of traps near the junction. We are using the new technique to probe the effects of different interface reconstructions, and defect densities. This work will be discussed in a future publication.

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