Observation of Midgap Interface States in Buried Metal/GaAs Junctions

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Second-order nonlinear optical spectroscopies reveal midgap interface states at buried metal/GaAs junctions, and demonstrate that these states are sensitive to interface preparation. In As-rich (Ga-rich) Au/GaAs n-type samples one (two) midgap resonance was observed. Similar resonances were exhibited in As/GaAs n-type samples, but were not present in metal/GaAs p-type systems. The sharp spectral features provide compelling evidence for the existence and symmetry of atomic displacement-induced defect states just below the buried interface.

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Interface states at metal/semiconductor junctions play an important role in controlling semiconductor device performance. For instance, Fermi level pinning and Schottky barrier heights are determined by these interface states [1,2]. In this paper we focus on the states associated with the *buried* metal/GaAs interface. Although there are a number of experimental observations consistent with the existence of midgap states in this system, there are very few direct spectroscopic measurements of interface energy levels. Some spectroscopic evidence for interface states has been derived from cathodoluminescence (CLS) [3] and inverse photoemission (IPS) [4], but these spectra are broad, and the measurements are not intrinsically sensitive to the buried interface. Other experiments have probed GaAs *surfaces*. For example, scanning tunneling microscopy (STM) was used to study As-related atomic defects on GaAs surfaces [5], and ultraviolet-photoemission spectra (UPS) have been used to study metal adsorbate-induced states in GaAs [6]. The lack of clean spectra from the buried interface, however, makes it difficult to challenge microscopic models about growth and defects in these and other systems.

In this Letter, we report investigations of interface states at metal/GaAs junctions by second-harmonic (SH) and sum-frequency (SF) spectroscopies [7]. Our experiments reveal interface states at metal/GaAs junctions and demonstrate that these states are sensitive to interface preparation. In contrast to CLS and IPS measurements, *sharp* resonant features were observed. The intrinsic interface sensitivity of second-order nonlinear optical spectroscopies enable us to suppress spectral contributions from the adjoining bulk media, resulting in more specific assignments of the spectral features, and a narrowing of the features by comparison to those observed with competing spectroscopies. Our observations provide strong evidence for the existence of atomic displacement-induced defect states at the buried metal/GaAs interface, and offer energy level and symmetry information that can be used to check theoretical predictions about this class of interface state [8].

In particular, Au/GaAs n-type systems exhibit a single midgap state in As-rich interfaces and two closely spaced midgap states in Ga-rich interfaces. As/GaAs n-type samples were observed to exhibit the same resonance as the As-rich, Au/GaAs n-type sample. On the other hand, no resonances were observed in metal/GaAs p-type systems within the same spectral region. After consideration of various three-step optical processes, we suggest that the transitions originate from the midgap states. Our observations are consistent with defect models involving the displacement of As and Ga atoms at the interface [8]. In fact, the spectra can be interpreted to yield direct information about defect state symmetries and relative energies. Three-wave mixing spectroscopy has been used with considerable success to probe buried interfacial features associated with new bonds [9], band profiles [10], and strain [11]. The present paper is the first to demonstrate *spectral* sensitivity to atomic defect states that arise near the junction. The experiments also suggest that the interfacial spectral features can provide information about the ratio of different substrate atoms at buried metal/semiconductor interfaces.

Our GaAs(001) samples were doped ($\sim 1 \times 10^{16}$ cm^{-3}) with Si (n type) and Be (p type). They were grown on an undoped GaAs substrate by molecular-beam epitaxy (MBE) at temperatures of ~580 °C, and with background chamber pressures of $\sim 3 \times 10^{-10}$ Torr. GaAs(001) exhibits a wide variety of surface reconstructions. These reconstructions are often related to the relative Ga to As ratio at the GaAs surface [12]. Reflection high energy electron diffraction (RHEED) measurements were performed on all samples to determine the surface reconstructions before growth of the Au epitaxial film. GaAs(001) samples were either As rich (2×4 surface reconstruction) or Ga rich (4×2 surface reconstruction) [13]. The ratio of As:Ga was 75%:25% (25%:75%) for the 2×4 (4×2) reconstruction. An 80 Å epitaxial Au film was then grown on the GaAs(001) surface with a surface temperature of ~400 °C. We confirmed the Au film was

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epitaxial by RHEED. We also grew amorphous, 80 Å As metal films. When such a sample is exposed to air, a fraction of the As film is converted into an oxide, but Auger spectroscopy confirmed that oxygen did not penetrate as far as the As/GaAs interface. Finally bulk GaAs(001) n- and p-type samples with native oxide overlayers of ~50 Å were also studied.

A 10 Hz Q-switched Nd:YAG pumped tunable optical parametric oscillator (OPO) was used as the fundamental SH generating light source for the measurements. The samples were irradiated at an incidence angle of 75°. Incident light pulses had a temporal duration of 10 nsec, and a fluence of ~1 mJ/cm^2. The fundamental (SH) photon energy range was from 0.68 to 0.78 eV (1.36 to 1.56 eV). The reflected SH power was measured as a function of OPO output light wavelength, and was normalized using a quartz reference plate. Sum-frequency generation (SFG) spectra were obtained by irradiating samples with the Nd:YAG beam at 1064 nm, and the tunable infrared beam using the same incidence angles and polarizations. All experiments were performed in air. In the p-in/p-out polarization configuration, with the crystalline [100] axis parallel to the plane of incidence, the bulk allowed GaAs(001) nonlinearity, $\chi^{(2)}_{xyz}$, was suppressed by $\geq 10^4$, thereby greatly enhancing our sensitivity to interface features [10]. Results obtained in p-in/p-out will hereafter be referred to as interface signals.

In Fig. 1, we exhibit measurements of interface second-harmonic generation (SHG) and SFG spectra from Au/GaAs n-type samples with different GaAs surface reconstructions (i.e., As rich and Ga rich). The interface spectra exhibit a single sharp peak at one-photon energy 0.715 eV for the As-rich Au/GaAs n-type sample, and two closely spaced peaks for the Ga-rich Au/GaAs n-type sample. The solid lines in the spectra from the Ga-rich Au/GaAs n-type sample represent a best fit to the data using Lorentzian line-shape functions. According to the fitting, the SH (SF) peak positions are 0.708 ± 0.014 eV (0.713 ± 0.014 eV) and 0.731 ± 0.014 eV (0.730 ± 0.014 eV), respectively. We believe that the low energy peak in the SHG (SFG) spectra at ~0.708 eV (0.713 eV), has the same origin as the single sharp peak in the As-rich Au/GaAs n-type system, while the high energy peak is a new feature resulting from the different interface preparation. All resonance features were confirmed to be one-photon resonances by comparison to SFG spectra. SHG and SFG experiments on As/GaAs(001) n-type samples within the same photon energy range, revealed a single one-photon resonance feature around 0.715 eV (see Fig. 2). Interestingly, in contrast to previous spectroscopic experiments [3–5], all of the observed resonances are sharp, suggesting a narrow distribution of states at or just below the buried interface.

There are two probable excitation processes that can be invoked to explain the one-photon resonance (see Fig. 3). Each process starts in a different initial state. In one case the three-step process originates from the top of the valence band [see Fig. 3(a)], and in the other case the process originates from the interface midgap state [see Fig. 3(b)]. Because the resonance energy is approximately half of the GaAs band-gap energy, double resonances arise in both cases, and SHG signals are stronger than SFG signals. Bulk SHG $\chi^{(2)}_{xyz}$ spectra have also been taken in the p-in/s-out polarization configuration [10]. Since bulk resonance features were not observed (see inset of Fig. 2), our assignment of these features to interfaces in the system was further corroborated.

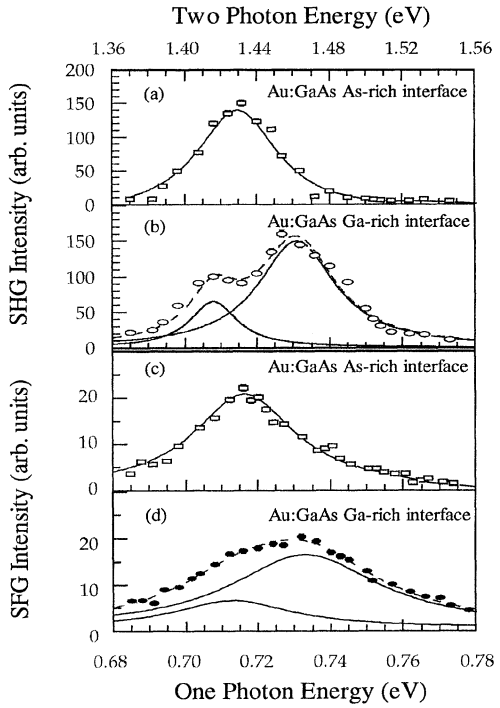

FIG. 1. Interface SHG and SFG spectra from Au/GaAs n-type samples. (a) SHG spectrum from As-rich Au/GaAs n-type samples. The solid line is a guide for the eye; (b) SHG spectrum from Ga-rich Au/GaAs n-type samples. The two solid lines are fitted using two Lorentzian line-shape functions, and the dashed line is the combination of the above two lines. The peak positions are estimated to be 0.708 ± 0.014 and 0.731 ± 0.014 eV, respectively. (c) SFG spectrum from As-rich interface sample. The solid line is a guide for the eye; (d) SFG spectrum Ga-rich interface sample. The two solid lines are fit using two Lorentzian line-shape functions, and the dashed line is the combination of the above two lines. The peak positions are estimated to be 0.713 ± 0.014 and 0.730 ± 0.014 eV, respectively.

Because the two possible excitation processes originate in different initial states, variation of carrier density in these initial states should affect the interface resonance spectra. To test this hypothesis we took spectra from metal/GaAs (p-type) samples within the same spectral region. In our analysis, we assumed that the energy levels at the interface are not changed by changes in bulk doping and overlayer oxidation [2]. This assumption is plausible for atomic displacement-induced defect states. However,

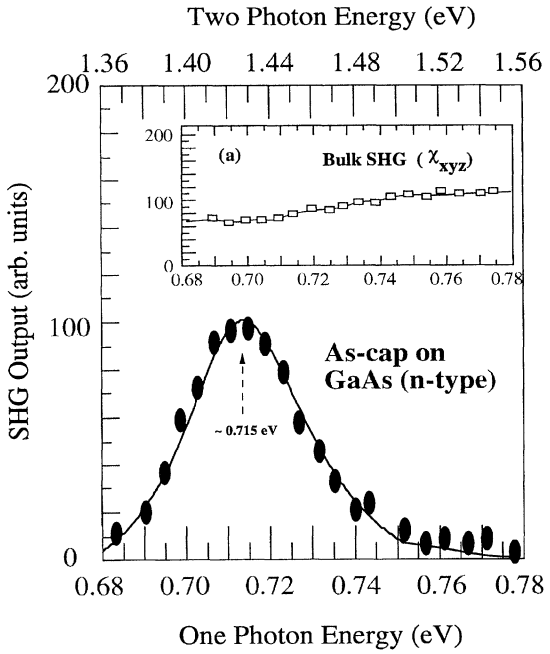

FIG. 2. Interface SHG spectra from the As capped GaAs n-type sample; the solid line is a guide for the eye. The inset (a) exhibits the bulk SHG spectrum from Au/GaAs n-type samples. Both As-rich and Ga-rich interface samples have the same bulk spectra.

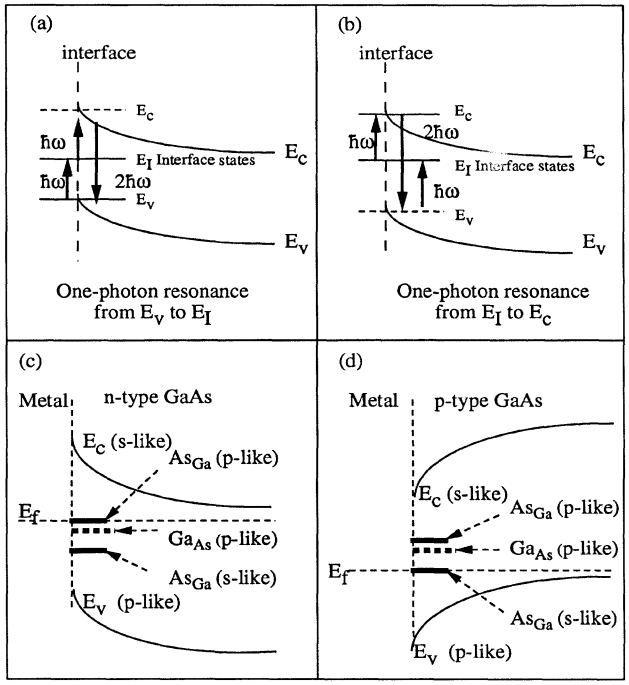

FIG. 3. Schematic of two most probable three-step optical processes giving rise to the one-photon resonance. (a) Time-ordered process starts in valence band, and is represented by $E_v \xrightarrow{\hbar\omega} E_I \xrightarrow{\hbar\omega} E_c \xrightarrow{2\hbar\omega} E_v$. (b) Time-ordered process starts from interface states, and is represented by $E_I \xrightarrow{\hbar\omega} E_c \xrightarrow{2\hbar\omega} E_v \xrightarrow{\hbar\omega} E_I$. (c) Schematic representation of As (As_{Ga}) and Ga (Ga_{As}) displacement defect state energies and symmetries in n-type GaAs/metal interfaces. (d) Same as (c) except in p-type GaAs/metal interface. E_c (E_v) denote conduction (valence) band energy minima (maxima), E_F denotes the Fermi level in these systems, and E_I denotes interface state energy.

the carrier occupation density in these states varies, since the Fermi level can shift with respect to the midgap levels. In p-type metal/GaAs systems these midgap states become empty as the Fermi level shifts towards the valence band maximum [3,14], and no resonance features are observed. The results suggest that the one-photon resonances in metal/GaAs n-type samples are due to the resonant transition from the occupied midgap states to the conduction band minimum. We conclude that the dominant three-step resonance processes start from midgap states. Later we show that these arguments are further supported by existing microscopic theories about defect levels near the interface.

The interface signals may contain contributions from the front metal surface, and higher-order bulk nonlinearities. To examine the contributions from the Au surface, we measured SFG and SHG spectra from a thick Au-epitaxial film (~5 μm) and found that SFG and SHG signals were below our noise level. Additionally, since the bulk nonlinear response of the Au epitaxial layer is expected to contribute similarly in both n- and p-type GaAs systems, the fact that no resonance features were observed in Au/GaAs p-type systems effectively rules out contributions from Au epitaxial films. The possibility of higher-order GaAs bulk contributions was 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 at least 2 orders of magnitude smaller than the interface signal [10]. In addition, the higher-order bulk terms contribute in the same way to metal/GaAs and oxide/GaAs systems, and no resonances in oxide/GaAs systems were observed. In total, these findings rule out higher-order bulk contributions as sources of the resonance features. The 0.715 and 0.731 eV resonance features most likely originate from the buried interface.

Our measurements of As/GaAs and Au/GaAs n-type samples exhibit a similar resonance at 0.715 eV, suggesting the common interface state may be related to excessive As atoms near the interface. On the other hand, the interface state at ~0.731 eV was found only at the Ga-rich interface in Au/GaAs n-type systems. This suggests that the latter interface state is related to the presence of excessive Ga atoms at the interface.

As a group these observations can be understood within a simple theoretical framework. A gradient, for example, in the chemical potential for As or Ga atoms can induce the migration of these atoms into the GaAs substrate. As

a result of relative concentrations of As and Ga atoms during growth, we might expect the formation of high concentration As atom displacement-induced defect states near the As-rich interface [2]. In this case the As atom sits in the Ga site in the interfacial region. Such As atom displacements are the first step in the production of several primary defect states in GaAs [2,5,15,16]. Two associated strongly bound energy levels with s-like and p-like symmetries, respectively, are predicted to lie near the middle of the band gap [see Figs. 3(c) and 3(d)] [8]. Similarly a high concentration of Ga displacement-induced defect states are expected for the Ga-rich interface. In this case, Ga atoms sit in As atom sites. A single strongly bound Ga displacement defect state has been theoretically predicted to have a p-like symmetry and an energy level near the middle of the band gap [8].

Our observations can be explained if we assume that the theoretical assignment of defect state relative energies and symmetries is correct [8], and that Ga-rich interfaces still contain some As defect states near the interface. In this case the n-type GaAs systems will experience Fermi-level pinning by the p-like defect states, while the p-type GaAs system will experience Fermi-level pinning by the s-like defect states (see Fig. 3). The observed resonances are derived by three-step processes that progress from occupied p-like defect states, to the s-like conduction band, to the p-like valence band, and then back to the original defect state. The last step is allowed as a result of weak strain- or field-induced interfacial state symmetry breaking. The model explains the observation of two resonance peaks in the Ga-rich interface, and it predicts no transitions in p-type GaAs systems since p-like states will be unoccupied. It also predicts new resonances in spectral regions not studied here, as a result of processes coupled to the s-like defect states. The very sharp spectra suggest that overlayer metal atoms displace the As or Ga, and that the detected atomic displacement defects occur in bulk GaAs just far enough from the interface so that their interaction with the metal overlayer free electron states is weak. Indeed the defect states probed must be sufficiently close to the interface to break symmetry, but sufficiently far from the interface to prevent spectral broadening through interactions with the metal. Qualitatively our spectra also suggest that the ratio (peak height or integrated area) of the two resonance peaks (0.715, 0.731 eV) can be related to the ratio of As:Ga defect states at the interface [17].

In conclusion, second-order nonlinear optical spectroscopies have revealed midgap interface resonance states at ~0.715 and ~0.731 eV, which may be associated, respectively, with As and Ga atomic displacements just below the buried interface. Within the confines of existing theoretical predictions about these states [8], our measurements corroborate predicted symmetries, relative energies, and the existence of these defect states.

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