Novel photovoltaic δ-doped GaAs superlattice structure

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An asymmetric δ-doped GaAs structure is described which exhibits novel photovoltaic effects and low-intensity nonlinear optics. Of particular interest in this kind of structure is the ability to design the electro-optical and nonlinear optical properties and the material response time over a wide range by appropriate design of the doping profile.

Several interesting superlattice structures have been created in recent years by doping GaAs with ultrathin layers of dopants at periodic intervals. Such doping is referred to as δ doping because charge densities of $\sim 10^{13}$ carriers/cm^2 can be achieved in dimensions comparable to a GaAs monolayer. These planes of charges then result in large electric fields in the intervening undoped GaAs regions which, in turn, result in bending of the valence and conduction bands. Optical excitation across the GaAs band gap gives rise to rapid free-carrier displacement in the electric fields. Many interesting optical effects, which have been observed in δ-doped superlattices, include absorption and luminescence at wavelengths longer than the GaAs band gap,[1] long excited carrier recombination times,[2] and quantization of electron and hole states confined in two-dimensional regions.[3]

In this letter we describe the first studies of asymmetric δ-doped GaAs which exhibit novel photovoltaic effects as well as interesting nonlinear optical behavior. Both the magnitude and response time of the nonlinearity can be tailored by appropriate design of the doping profile. Alternating planes of *p* dopants (Be) and *n* dopants (Si) were grown in otherwise undoped GaAs by gas source molecular beam epitaxy (MBE) such that the distance from *n* to *p* planes in the growth direction is different from the distance from *p* to *n* planes as shown in Fig. 1(a). In this case, pairs of planes of opposite charge are separated by 75 Å with subsequent planes separated by 500 Å, thereby creating a dipolar superlattice with a period of 575 Å. The corresponding sawtooth-shaped band structure is shown in Fig. 1(b). It is immediately evident that the symmetry of such a structure is lower than that of symmetric δ-doped structures previously investigated. They belong to a piezoelectric and pyroelectric crystal class and should exhibit electrical and nonlinear optical behavior characteristic of polar space groups.[4] Of special interest in this letter is that optical excitation results in photovoltaic effects similar to those of polar dielectrics. However, the ability to tailor the local fields, the asymmetry, and the dimensions of the superlattice lends special importance to this new class of materials for electro-optic applications.

Optical excitation of the superlattice with light of energy greater than the GaAs band gap results in the spatial separation of electrons and holes as shown in Fig. 1(c). The most probable recombination path is by tunneling-assisted radiative recombination to the neighboring superlattice period [path *A* in Fig. 1(c), note the proximity of electrons and holes], rather than path *B* within the same superlattice period. (We define a superlattice period as the separation of potential maxima.) Thus, light emitted upon recombination is at wavelengths longer than the GaAs band gap. The optical emission spectrum for the δ-doped superlattice structure of Fig. 1 is shown in Fig. 2. Spectra were taken at 15 K with cw argon ion laser excitation at 0.5145 μm and a germanium detector. With relatively low excitation intensity, $I_p = 3.6$ W/cm^2, the luminescence is observed to peak near 1.5 μm in the infrared. At higher intensities, the luminescence peak shifts to higher energies as photocarriers screen the internal fields due to δ doping. At the highest intensities, $I_p \sim 800$ W/cm^2, the luminescence peaks close to the GaAs band edge at 0.87 μm. Qualitatively, this behavior is similar to the intensity dependence of symmetric δ-doped superlattices,[2] but the magnitude of the observed intensity-dependent wavelength shift is particularly large in this case. The origin of the double peak observed near 0.9 μm at the highest intensities is not understood. It should be pointed out, however, that absorption of the 5145 Å pump beam in the superlattice results in considerable variation of the excitation density throughout the structure and the luminescence shown in Fig. 2 is the total emission from layers screened to a different degree.

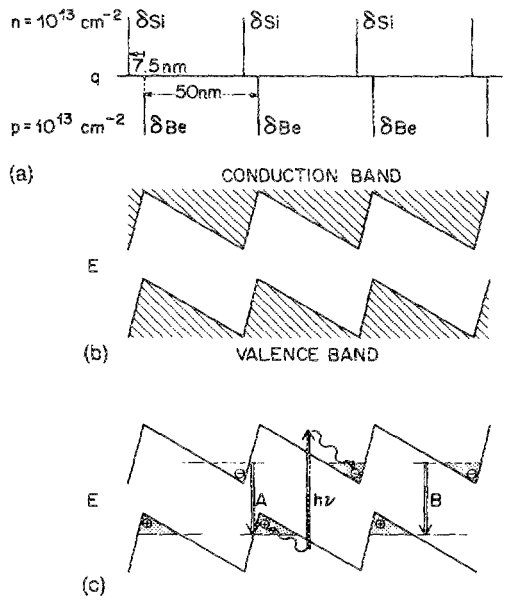

FIG. 1. Schematic diagrams of (a) the doping profile, (b) the sawtooth band structure, and (c) free-carrier excitation, charge transfer, and recombination of a δ-doped GaAs sample.

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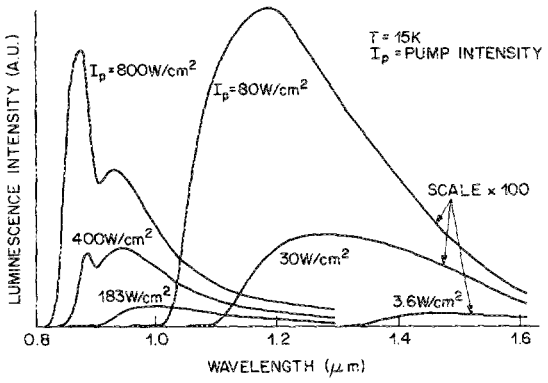

FIG. 2. Optical luminescence spectra (15 K) of the asymmetric δ-doped GaAs sample of Fig. 1 for various pump intensities I_p.

Optical excitation in polar materials generally results in either transient displacement currents for localized excitation[5] or bulk photovoltaic effects[6] for free-carrier excitation due to the local asymmetry at the absorbing centers. Transient currents occur when charge displacement upon recombination is equal and opposite to that created upon excitation resulting in zero net current flow, as observed in compositionally graded $Al_xGa_{1-x}As$ sawtooth superlattices.[7] Photovoltaic effects, on the other hand, imply a charge transfer following excitation and recombination, resulting in net current flow. In asymmetric δ-doped superlattices, it is possible to generate either transient displacement currents or continuous photovoltaic currents depending on the design of the structure. In the present case, the superlattice was designed with a broad region for photocarrier displacement and a narrower region for photocarrier recombination by tunneling to the neighboring well. The overlap of the relaxed electron and hole wave function for transition A to the neighboring well [see Fig. 1(c)] is significantly greater than that for recombination in the same well via transition B as discussed below. It is clear upon examination of Fig. 1(c) that the photovoltaic current resulting from optical excitation across the GaAs gap is

$$J = fNe\Lambda,$$

where Λ is the superlattice period, e is the electronic charge, N is the free-carrier excitation rate ($N = \alpha I_p/h\nu$), f is the probability of charge transfer to the neighboring superlattice period, and α is the absorption coefficient of the superlattice. The factor f is an asymmetry parameter which is a measure of the difference in probability of recombination via path A or path B in Fig. 1(c), as well as the difference in absorption cross section in the two regions of different internal field.

The superlattice structure of Fig. 1 was grown on an n-GaAs substrate, with a 5000 Å n^+-GaAs buffer layer below the superlattice and a 100 Å n^+ cap above the superlattice. Gold-germanium alloy contacts were made to the substrate and cap. In the top electrode, a small window of semitransparent conducting gold was used for irradiation of the sample. This structure was thus electrically symmetrical except for the superlattice region thereby minimizing any junction photovoltaic effects from the buffer layers.

The photovoltaic response of the sample (i.e., no applied field) was measured as a function of wavelength using low-intensity incoherent light (10 mW/cm^2) from a monochromator. The spectral response, at room temperature, is shown in Fig. 3. Current response is observed well below the GaAs band edge out to a wavelength beyond 1.2 μm. The sign of the photocurrent was consistent with the superlattice asymmetry, but opposite to that expected from any Schottky barrier effects which might arise from an imperfect upper ohmic contact. At wavelengths shorter than 0.82 μm, the photocurrent decreased, presumably due to absorption in the GaAs cap layer near the top electrode. The spectral response below the GaAs band gap is readily understood in terms of the decreasing overlap of electron and hole states throughout the entire low-field region of the superlattice. As discussed below, transitions across the minimum gap in the high-field region (observed in luminescence) do not contribute to the photovoltaic spectrum, since these do not result in charge transfer to the neighboring well.

Both the photocurrent response and luminescence decay time of the superlattice were studied with $\sim$50 ns duration pulsed excitation from a Nd:YAG laser at 1.06 and 0.53 μm. The time scale is long compared with the intrinsic recombination time of GaAs. Since the pulse energy required for reliable relaxation time studies was >10 μJ/cm^2, the initial photocarrier density was sufficient to screen the internal fields in the superlattice. Thus the photocarrier decay kinetics exhibited complex nonexponential behavior due to the time varying band structure. Such behavior has been studied in other staggered alignment superlattice structures.[8] At short times (<100 ns) following excitation (at high carrier densities), the luminescence is primarily at short wavelengths (<1.0 μm) due to direct electron-hole recombination. At longer times (>1 μs), the emission wavelength is primarily at longer wavelength due to tunneling-assisted recombination. This long lifetime is consistent with the screening effects observed in luminescence in Fig. 2 even at the lowest intensities (3.6 W/cm^2), since the estimated photocarrier density in this case is 10^{12} cm^{-2} per superlattice period, or 10% of the space-charge density created by δ doping.

The photovoltaic current response measured under the same circumstances using short pulse excitation is similar to the long-wavelength photoluminescence decay with a non-

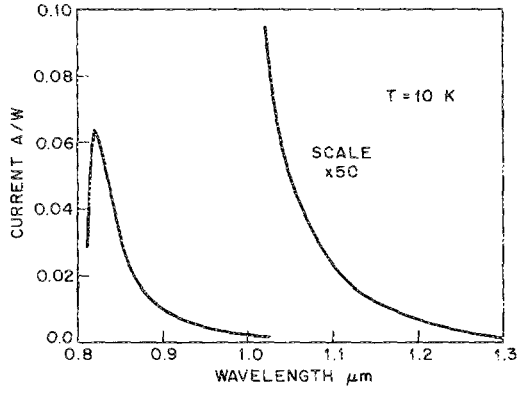

FIG. 3. Photovoltaic response spectrum of the sample of Fig. 1 at low intensities.

exponential relaxation time of 1–2 μs. Although the similarity of these relaxation times indicates similar electronic origins of the two processes, identical behavior is not expected. Recombination within a superlattice period (type B recombination shown in Fig. 1) will contribute to the measured optical decay, but not to the current response.

Very similar experimental results are obtained at low temperatures (6 K) indicating that competitive nonradiative processes and phonon-assisted processes play at most a minor role in the carrier dynamics of this superlattice.

To obtain an estimate of the relative transition probability of the two recombination processes labeled A and B in Fig. 1, we used variational wave functions of the form

$$\psi_1(z) = c(1 - \alpha_1 z)e_1^{\alpha} \quad \text{for } z \leqslant 0,$$
$$\psi_2(z) = c(1 + \alpha_2 z)e_1^{\alpha} \quad \text{for } z \geqslant 0,$$

to describe the $n = 0$ state of electrons and holes in an asymmetric V-shaped potential well. The origin, $z = 0$, is the minimum of the V potential and α_1 and α_2 are the trial parameters of the variational wave function. Approximate values of the exponential decay parameters α_1, and α_2 for the high-field and low-field regions were obtained by minimization of the energy expectation values for the specific asymmetric potential shown in Fig. 1. For electrons

$$(\alpha_1^e)^{-1} \simeq 10 \text{ Å} \quad (\alpha_2^e)^{-1} \simeq 34 \text{ Å},$$

and for holes

$$(\alpha_1^h)^{-1} \simeq 5 \text{ Å} \quad (\alpha_2^h)^{-1} \simeq 18 \text{ Å}.$$

Using these values, the relative overlap $\int \psi_1 \Psi_2 dz$ of electrons and holes in the high-field (transition A) and low-field (transition B) regions is 350:1. That is, the probability of recombination of electrons and holes in neighboring superlattice periods is 350 times greater than that for recombination in the same period. At high carrier densities this ratio decreases as the internal fields are screened.

It is found from the analysis that the minimum radiative transition energy is 0.67 eV or 1.84 μm, consistent with the long-wavelength emission observed at low intensities in Fig. 2 out to the limit of sensitivity of the germanium detector. It is also found that for wavelengths shorter than ~ 1.1 μm, absorption in the low-field region is dominant while for wavelengths longer than 1.1 μm, absorption in the high-field region is dominant. For this reason the photovoltaic response decreases rapidly for wavelengths beyond 1.1 μm.

Asymmetric δ-doped superlattices thus offer a great deal of flexibility for the design of electro-optic and other nonlinear optical devices. The optical absorption properties and the carrier recombination rates can be designed independently by appropriately designing the different regions of the superlattice. Indeed, it would appear feasible to design a system with nearly degenerate electron and hole states in the high-field region of the superlattice with extremely rapid electron-hole recombination. This ability to design structures, with broad spectral response, weak temperature dependence, large free-carrier displacement, and rapid or slow recombination is important for future photonic devices. The ability to design such structures in single component semiconductors rather than multilayer heterostructures is particularly important since these principles are equally applicable to silicon or germanium structures where lattice-matched heterostructures do not exist.

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