High-resolution optical detection of electron spin resonance in epitaxial semiconductor layers by coherent Raman spectroscopy

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We describe the application to semiconductors of a microwave-frequency optical heterodyne technique that enables electron-spin-resonance spectra to be detected through coherent Raman scattering. The technique is sufficiently sensitive to detect spectra from epitaxial layers and has the added advantage of optical selectivity. We demonstrate its effectiveness with studies of a ZnSe epitaxial layer in which there is a variation in strain. The spin-resonance linewidths are sufficiently narrow for the gyromagnetic ratio to be determined with a precision of 1 part in 10^4 and, as the laser is tuned to resonance with differently strained parts of the material, the g value changes at a rate of approximately 0.4 eV^{-1}. We have carried out the experiment in both transmission and reflection geometries and the technique promises to be of wide applicability.

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It has long been recognized that the determination of gyromagnetic ratios (g values) and other spin-Hamiltonian parameters provides considerable insight into the behavior of electrons in condensed matter. In semiconductors, for example, such parameters are sensitive to the band structure, to strain, and to the state of binding of the electron. In principle, the most direct method for such measurements is electron spin resonance (ESR), which has been used extensively over many years to investigate dopant and defect states in bulk specimens. However, mainstream interest in semiconductors has now moved from bulk crystals to epitaxial structures and the sensitivity of ESR in its conventional form is, unfortunately, sufficient only for the study of relatively highly doped specimens. Furthermore, conventional ESR cannot distinguish between signals obtained from different parts of the heterostructure. An alternative approach is necessary. The purpose of the present paper is, therefore, to describe an optical detection scheme based on coherent Raman scattering that makes it possible to observe ESR in the small active sample volumes of epitaxial layers and heterostructures. The technique has the important advantage of optical selectivity and promises to be of wide applicability.

The approach is illustrated by the three-level energy diagram of Fig. 1(a). The lower levels represent the two Zeeman components of the ground state of the center under investigation, and, in the simplest case, are split in a magnetic field B by an amount $g\mu_B B$, where μ_B is the Bohr magneton. The Zeeman splitting can be measured directly in standard (noncoherent) spin-flip Raman scattering (SFRS) experiments (e.g., Refs. 1–4). The Raman shifts are measured using a dispersing spectrometer or a Fabry-Perot interferometer: the accuracy is usually limited by the laser linewidth and by the strength of the available magnetic field and g values determined in this way are typically quoted to an accuracy of a few percent. An important aspect is that the scattering cross section is enhanced considerably when the laser is tuned to coincide with the relevant excitonic transition, as indicated in Fig. 1(a). Since the energies of excitons bound to different scattering centers are not the same, SFRS as a function of laser wavelength is highly selective.

The optically detected ESR experiment reported here differs significantly from the standard SFRS technique. The additional feature [Fig. 1(b)] is that excitation of the magnetic-resonance transition $|1\rangle \rightarrow |2\rangle$ with microwave radiation imposes a coherence in the ''spin-flip'' scattered light.[2,3] The resulting constructive interference between Raman waves originating at different centers creates a temporally and spatially coherent signal beam. Coherent Raman scattering thus occurs with the Raman frequency shift being equal to the microwave frequency.[2,3,5] The amplitudes of the coherent Raman waves are linearly related to the microwave-induced precessing magnetization that occurs at magnetic resonance.

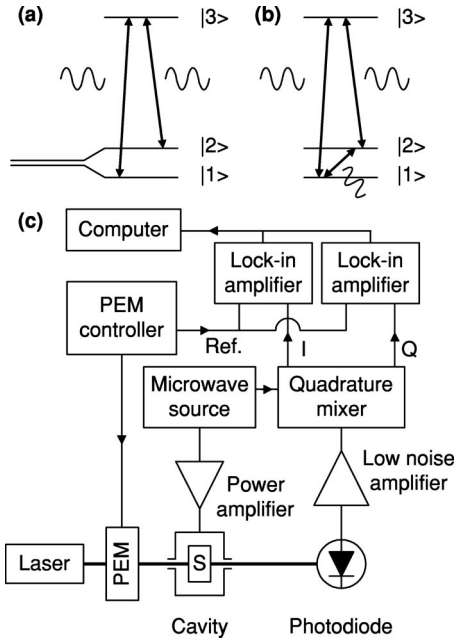

FIG. 1. (a),(b) Energy-level diagrams, respectively, illustrating normal (noncoherent) spin-flip Raman scattering and microwave-assisted coherent scattering. States 1 and 2 represent the two spin states of the electron and are separated in energy by $g\mu_B B$. (c) Schematic arrangement of the equipment used. The magnetic field is normal to the direction of the laser beam and the specimen is at 2 K. Two lock-in amplifiers are used to monitor the absorption and dispersion phases of the signal simultaneously.

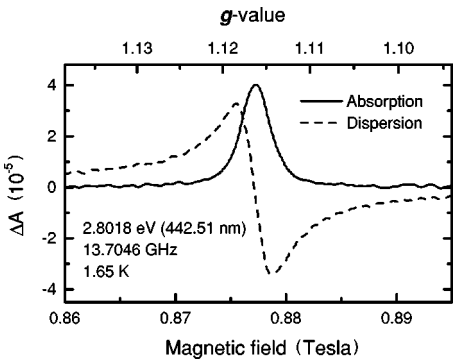

FIG. 2. The absorption and dispersion components of the CR-ESR spectrum from a ZnSe epitaxial layer. The incident microwave and laser powers were, respectively, 100 mW and 40 mW.

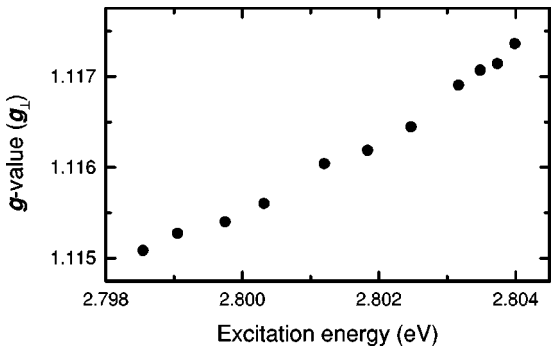

FIG. 3. The dependence of the measured value of $g_\perp$ on the laser energy.

Further, the phase difference between the exciting microwave field and the precessing magnetization is directly reproduced in the coherent Raman waves. Measurement of the amplitude and phase of the Raman waves thus provides the same information as conventional ESR absorption and dispersion measurements and the behavior can be treated using well-established theories.[6,7]

The distinguishing feature of our experiment is that, to measure the amplitude and phase of the coherent Raman waves, we use an optical heterodyne detection scheme, in which the Raman radiation beats against the copropagating laser in a high-speed photodetector. Such an approach has been employed previously where the frequencies of the optical signal and laser waves differ by radio frequencies (<1 GHz), e.g., in experiments on color centers in diamond,[8] on atomic vapor hyperfine transitions[9] and nuclear quadrupole transitions of lanthanide ions in crystals.[10] More recently, we have built an optical heterodyne detection instrument operating at a much higher frequency (13.7 GHz) that has been used to measure the first coherent Raman ESR (CR-ESR) spectra of transition-metal ions, initially in $Cr^{3+}:Al_2O_3$ (Ref. 11) and later in metalloenzymes.[12] Here we report the application of the technique to epitaxial semiconductor layers.

The experimental arrangement is shown in Fig. 1(c). The specimen is placed in a rectangular TE_{012} mode 13.7-GHz resonator with optical transmission in a direction along the specimen growth axis and perpendicular to the field produced by a superconducting magnet. Liquid helium at 1.7 K is allowed to enter the resonator, which is excited at a continuous microwave power of the order of 100 mW. Radiation from an ultraviolet-pumped Coherent 599 continuous-wave dye laser passes through the specimen and is focused on to a high-speed InGaAs Schottky photodiode. For the transmitted laser and coherent Raman radiation to interfere (that is, for the laser to act as a local oscillator[5,13]) it is necessary to excite with circularly polarized light. The resulting 13.7-GHz beat signal is detected using a low noise coherent microwave receiver similar to the ''bridge'' of a conventional ESR instrument and use of a quadrature mixer allows the simultaneous measurement of both the absorptive and dispersive components. Changing the sense of polarization of the laser from left to right changes the sign of the signal, so that polarization modulation (at 50 kHz), such as the magnetic-field modulation typically used in conventional ESR instruments, allows the use of lock-in detection. As in conventional ESR, we sweep the magnetic field, rather than the microwave frequency: however, since there is no field modulation, the signals are not differentiated with respect to field as is usual in ESR. The data may be plotted conveniently as the modulation ΔA of the sample absorbance A, which is of the form $A=A_0+(\Delta A/2)\sin(\omega_1 t)$, where $\omega_1/2\pi$ is the microwave frequency and A_0 is the average absorbance.

The specimen studied was an undoped 0.8-μm epitaxial layer of ZnSe grown by metal-organic vapor phase epitaxy (MOVPE) on GaAs and subsequently removed from the substrate and glued to a fused silica disc. The photoluminescence spectrum shows a strong line due to recombination of excitons bound to neutral donors (the I_2 line).[14] The line is shifted from that in cubic ZnSe because of the biaxial compressive strain caused by the difference in thermal contraction of the epilayer and the silica and is also broadened because of the nonuniformity of the strain. When the laser is set to resonance with I_2, strong spin-flip transitions are readily observed in the conventional SFRS spectrum, leading to a g value of 1.12 ± 0.03.

Both phase components of the CR-ESR spectrum are shown in Fig. 2. At the microwave power level available, the signals are not saturated. Their intensity is a strong function of the laser tuning and they are observed only when the laser is close to resonance with the I_2 line. Of note is the linewidth (2 mT) of the CR-ESR signal, which is sufficiently narrow to provide a precision of ±0.0001 in the g value. Expressed in energy units, the linewidth is about 10^{-4} meV, very much smaller than the resolution (~0.1 meV) typical of standard SFRS spectroscopy.

This high resolution of the experiment reveals that the exact g value is in fact a function of laser wavelength, as shown in Fig. 3. The g value of electrons in shallow states in ZnSe has been analyzed in detail (e.g. Ref. 15, and references therein) and is well described by five-band $\mathbf{k}\cdot\mathbf{p}$ theory. It has also been pointed out[16] that *changes* in the g value caused, for example, by strain or quantum confinement can be dealt with by considering only the leading terms that arise from the three-band theory, which, for the component $g_\perp$ of the g tensor in the plane of the epilayer, gives[17]

$$g_{\perp} = g_0 - \frac{2E_P}{3}\left[\frac{1}{E_{lh}} - \frac{1}{E_{so}}\right], \tag{1}$$

where E_{lh} and E_{so} represent the magnitudes of the energy separations of the conduction band from the light-hole and the spin-orbit split-off valence bands, respectively, and where E_P ($=24.3$ eV) (Ref. 15) is the interband momentum matrix element (in energy units). E_{lh} and E_{so} can be expressed as functions of the biaxial strain and deformation potential constants[18,19] and lead to the prediction that $dg\perp/dE_{hh} = 3.3$ eV^{-1}. This is around an order of magnitude larger than we observe experimentally and this discrepancy is not removed by using five-band theory. Our data, therefore, present a challenge to current band-structure models. There are several other effects that may introduce a correlation between g factor and excitation energy (e.g., band nonparabolicity, variation of donor species, varying overlap between adjacent donor wave functions) and the determination of the relative significance of these will require further study. The essential point is that the g-factor variation demonstrated here would be undetectable by other techniques.

We now turn to sensitivity considerations. Microwave-induced coherent Raman scattering has been observed using conventional Fabry-Perot detection by Romestain and co-workers.[3,2] Based on their analysis, one obtains the following expression for the sideband power P_S relative to the laser power P_L incident on the detector:

$$\frac{P_S}{P_L} = \frac{1}{4}\left(\frac{d\sigma}{d\Omega}\right)\frac{\lambda^2 N^2 \sigma_x^2 L^2}{\epsilon_s'} = \alpha^2 N^2 L^2, \tag{2}$$

where $(d\sigma/d\Omega)$ is the SFR scattering cross section, λ is the wavelength, ϵ_s' is the optical dielectric constant, N is the concentration of scattering centers, and $g\mu_B\sigma_x/2$ is the transverse magnetization generated by the microwaves. In Eq. (2) we have assumed that the specimen thickness L is small. For CdS excited at 488 nm, which is partly in resonance with the I_2 line in that material, and for a specimen with $L = 1$ mm and $N = 2\times10^{17}$ cm^{-3} with saturating microwave power, it was found[2,3] that Eq. (2) gave $P_S/P_L \approx 0.1$ (in reasonable agreement with experiment) so that α is about 10^{-17} cm^2.

Detection of such a large change is well within the scope of a Fabry-Perot system. The problem with epitaxial materials is, however, the appearance of the factor L^2 in Eq. (2). In our case, $L \approx 1$ μm, immediately requiring a factor of 10^6 increase in detected power sensitivity, which becomes very difficult to achieve with a Fabry-Perot system. The appearance of the factor N^2 imposes further demands, especially if the specimen is strained nonuniformly so that the number of scattering centers in resonance with a particular wavelength is reduced.

It is here that the sensitivity of the heterodyne technique becomes vital. The performance of optical heterodyne receivers for detection of ESR has been discussed by Bingham *et al.*[5] The signal is proportional to the amplitude of the Raman field multiplied by the amplitude of the unshifted laser field (i.e., the local oscillator). At sufficiently high laser power, the minimum detectable number of Raman signal photons in a given data acquisition period is of the order of the reciprocal of the photodetector quantum efficiency. Although this shot-noise limited performance is not quite reached in the present experiment, a minimum detectable Raman wave power of the order of 10^{-14} mW can be expected with a 0.1 mW local oscillator.[5] This is still very much better than can be achieved even by multipass Fabry-Perot systems. For example, in CdS with $L = 1$ μm, using the value of α quoted above, it should be possible to detect (3×10^{14}) cm^{-3} scattering centers. This value will fall with more laser power or a less absorbing sample. A sensitivity of the order of 10^{13} cm^{-3} centers should be possible before photoreceiver damage occurs.

The signals observed in ZnSe (Fig. 2) represent changes in absorbance of the order of $\Delta A = 4\times10^{-5}$, which corresponds to a ratio of Raman sideband power to the mean transmitted power of the order of 10^{-10}. We estimate that the precessing effective spin parameter σ_x in our experiment is similar to the CdS experiment,[3,2] and since the other parameters for ZnSe and CdS can be expected to be similar, an estimate for N of about 10^{16} cm^{-3} is obtained. However, this is likely to be an underestimate, possibly by an order of magnitude, since the exciton linewidth in our particular specimen is significantly broadened (full width at half maximum of about 5 meV) by the nonuniform strain that leads to the spread in g values shown in Fig. 3. This estimate of a donor concentration in the region of 10^{16} to 10^{17} cm^{-3} is consistent with values typical of nominally undoped ZnSe specimens produced by MOVPE.[20]

It is also interesting to contrast the sensitivity with that for conventional ESR. Our specimen volume is approximately 10^{-6} cm^{-3}, so that there are of order 10^{10}–10^{11} spins present. Conventional ESR instruments are typically quoted as having sensitivities (at 300 K) of 10^{12} spins for a 1 mT linewidth and 100 mW of microwave power. Although this improves at low temperatures, possibly by a factor of 100, depending on relaxation times, it is clear that conventional ESR signals at this doping level would be at the limits of instrumental sensitivity. Furthermore, there would be no differentiation between the centers that give the range of g values seen in Fig. 2 and the linewidth would be at least a factor 2 greater.

Further insight into the experiment comes from the semiclassical picture, in which the magnetization precesses about the magnetic field at the Larmor frequency and, at magnetic resonance, is driven into a disk.[6,7] Circularly polarized light incident in the plane of the disk experiences an oscillating circular dichroism and is thus amplitude modulated at the microwave frequency.[21] Advances in optical detectors and microwave amplifiers now make it possible to detect this modulation.

To summarize, we have reported the application of optical heterodyne detection of ESR to a semiconductor and demonstrated that the technique is sufficiently sensitive for the study of epitaxial layers. The linewidths are those expected in conventional ESR and both the real and imaginary phases of the signal can be detected. Here we have demonstrated the

approach by studying electrons trapped at donors in a simple epitaxial layer of ZnSe. In a separate experiment, we have also found that the measurements can be carried out in reflection geometry, which obviates the need to remove substrates. The technique should, therefore, be widely applicable to more complicated heterostructures. The optical selectivity enables the *g* values to be correlated with the optical transition energy, thus providing information that presents new challenges to existing theories.

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