

Energy-resolved electron spin dynamics at surfaces of *p*-doped GaAs

H. C. Schneider,¹ J.-P. Wüstenberg,¹ O. Andreyev,¹ K. Hiebner,¹ L. Guo,^{1,*} J. Lange,¹ L. Schreiber,² B. Beschoten,² M. Bauer,¹ and M. Aeschlimann¹

¹Physics Department, Kaiserslautern University, 67653 Kaiserslautern, Germany

²II. Physikalisches Institut, RWTH Aachen, and Virtual Institute for Spin Electronics, Templergraben 55, 52056 Aachen, Germany

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Electron-spin relaxation at different surfaces of *p*-doped GaAs is investigated by means of spin, time, and energy-resolved two-photon photoemission. These results are contrasted with bulk results obtained by time-resolved Faraday rotation measurements as well as calculations of the Bir-Aronov-Pikus spin-flip mechanism. Due to the reduced hole density in the band bending region at the (100) surface the spin-relaxation time increases over two orders of magnitude towards lower energies. At the flat-band (011) surface a constant spin relaxation time in agreement with our measurements and calculations for bulk GaAs is obtained.

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In recent years, much experimental and theoretical work has been focused on the control and manipulation of the electronic spin degree of freedom independently of its charge, with the ultimate goal of spintronics devices, in which the electron spins are the carriers of the information.¹ The limiting factor for the usefulness of the information encoded in a spin-polarized current in a nonferromagnetic semiconductor is the relaxation of the spin polarization, which is caused by a variety of interaction mechanisms.² In bulk GaAs, the relaxation of optically induced spin polarizations has been studied intensely for more than 30 years. Early work has led to the identification of several mechanisms that destroy the spin polarization, and good agreement between experiment and theory was found on the level of numerical and experimental accuracy available at that time.³ In recent years, there has been renewed experimental and theoretical interest in spin relaxation, with many experimental studies focusing on undoped and *n*-doped semiconductors.^{4,5} Early results for *p*-doped GaAs were obtained by means of hot photon luminescence and the Hanle effect.⁶ Surfaces and interfaces, such as Schottky barriers, originally received comparatively little attention.^{7,8} More recently, however, interfaces have been studied because of their importance for spintronics device applications where efficient electrical spin injection from a ferromagnetic metal or half-metal through a Schottky barrier into the semiconductor is of utmost importance.⁹ The difficulty of efficient spin injection has stimulated interest in a fundamental understanding of spin-flip scattering at semiconductor surfaces and interfaces, e.g., at step edges.¹⁰

The purpose of this paper is the investigation of electron spin relaxation in *p*-doped GaAs and the unambiguous identification of surface effects on the electron spin relaxation. Using a spin, energy, and time-resolved photoemission technique¹¹ we study the room-temperature spin-dependent electron dynamics at two surfaces with different characteristics:¹² the (100) surface with pronounced band bending and the cleaved (011) surface, for which we expect flat-band conditions. To obtain a complete picture of the spin relaxation at surfaces as compared to the bulk we have also measured bulk spin relaxation times by time-resolved Faraday rotation (TRFR) on identical samples. Furthermore, we nu-

merically evaluate for the first time the full momentum-dependent room-temperature bulk spin-relaxation rate for the Bir-Aronov-Pikus¹³ (BAP) electron spin-flip mechanism due to the electron-hole exchange interaction.

One should stress that we experimentally and theoretically study the dynamics of the *incoherent*, energy resolved, microscopic spin polarization $P = (n_{\uparrow} - n_{\downarrow}) / (n_{\uparrow} + n_{\downarrow})$ defined in terms of the transient, energy, or momentum-dependent electron distributions for spin-up (n_{\uparrow}) and spin-down (n_{\downarrow}) electrons. The dynamics of this microscopic spin polarization determines the relaxation of the macroscopic spin polarization, which is often described by a phenomenological (longitudinal) T_1 time. We therefore refer to the decay of the electron spin-polarization simply as spin relaxation. The experimental and theoretical results on spin relaxation presented here are obtained without external magnetic fields, and should therefore not be confused with the dephasing of *coherent* spin dynamics under the influence of magnetic fields, whose macroscopic counterpart is a (transverse) T_2 time.

At GaAs surfaces and GaAs/metal interfaces a Schottky barrier exists, in which the Fermi level pinning causes a band bending downward of magnitude up to 0.6 eV in *p*-doped GaAs.¹² For the experimental determination of the spin relaxation in the band bending region, we use a time-domain pump-probe approach known as time-resolved two-photon photoemission (TR-2PPE) to investigate excited electron dynamics with femtosecond time resolution. In our setup, a circularly polarized pump pulse with a photon energy just above the bulk band gap [process (1) in Fig. 1] can excite spin polarized electrons well in the bulk because of its penetration depth of several 100 nm. A probe pulse with a higher photon energy and smaller penetration depth (several 10 nm) removes electrons close to the surface [process (3)] after a time delay τ , during which the electrons have traveled towards the surface and undergone both momentum and spin-flip scattering processes [process (2)]. The kinetic energy of the photoemitted electrons together with their spin polarization is directly measured in a spin-sensitive low-energy electron diffraction (SPLEED) detector.¹⁴ One of the advantages of this technique is that it yields the energy-resolved spin

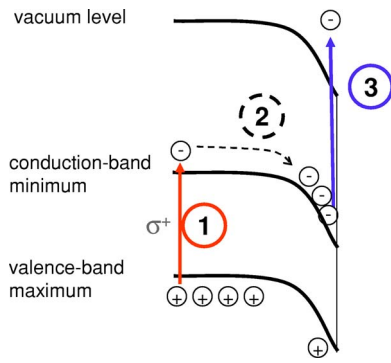


FIG. 1. (Color online) Two-photon photoemission process at a surface region with band bending involving: (1) the excitation of spin-polarized electrons by the polarized pump pulse away from the surface, (2) the scattering of electrons into low energy states in the band-bending region, and (3) the photoemission process from the surface due to the probe pulse with time delay τ . The hole density at the surface is reduced due to the hole band bending.

polarization $P(E, t)$ independently of the electron density. Electronic transitions due to, e.g., carrier-carrier scattering, or electron-hole recombination that reduce the carrier concentration in the investigated energy interval only result in an increased statistical error in the measured spin polarization.

Our TR-2PPE setup employs a Ti:sapphire laser at 82 MHz that yields linearly polarized light pulses of 50 fs full width at half maximum (FWHM) with a pump photon energy of 1.55 eV [process (1) in Fig. 1]. A fraction of the light is frequency doubled, leading to a probe photon energy of 3.1 eV [process (3) in Fig. 1]. The fundamental (pump) pulse is circularly polarized by a quarter-wave plate whereas the frequency-doubled (probe) pulse remains linearly p polarized. The two pulses are mechanically delayed with respect to each other using a Mach-Zehnder interferometer. The collinear pulse pair is focused on the sample surface within a UHV chamber. As sample we use a p -doped GaAs crystal with doping concentration (acceptor: zinc) $N_A = 3.6 - 7 \times 10^{18} \text{ cm}^{-3}$ both in (100) and (011) orientation. Prior to the measurements, the sample was treated with a small amount of cesium, thus leading to a well-defined Fermi-level pinning and a lowered work function of about 3.2 eV. The excited electron densities were about 10^{16} cm^{-3} .

Figure 2 shows normalized spin-integrated photoemission signals, i.e., the number of detected electrons at a fixed kinetic energy, for the GaAs (100) surface (pronounced band bending) and the (011) surface (essentially flat-band conditions). The electronic energies are $E - E_{\text{cbm}}^0 = -1.0, -0.9, -0.7,$ and -0.4 eV measured with respect to the bulk conduction-band minimum (CBM) E_{cbm}^0 . A time-independent background due to electrons photoemitted by multiphoton processes has been subtracted in the curves in Fig. 2. The spike around zero time delay is due to the photoemission of unpolarized electrons during the overlap of pump and probe pulses. For positive time delay τ , the 2PPE signal monitors the population dynamics at the surface. In the band-bending region of the (100) surface at $E - E_{\text{cbm}}^0 = -1.0 \text{ eV}$, the 2PPE signal in Fig. 2(a) indicates a rising electron population over 5 ps. For the next higher energy in the conduction band, this

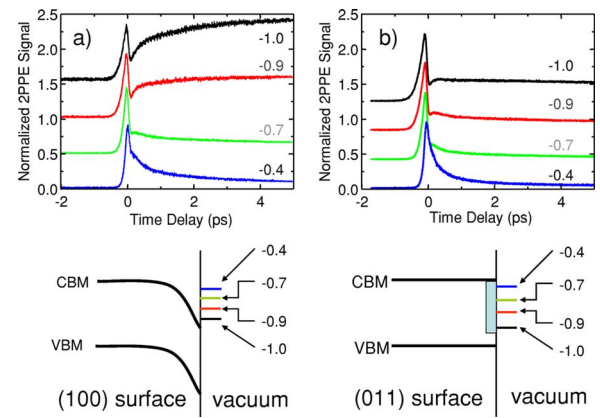


FIG. 2. (Color online) Normalized 2PPE signal vs time for different electronic energies at the GaAs (100) surface (a) and (011) surface (b). The corresponding band profiles displaying the conduction-band minimum (CBM) and the valence-band maximum (VBM) are sketched in the lower panel. Energies indicated in this figure are in units of eV and are measured with respect to the bulk CBM.

increase is less pronounced, and for the conduction-band states at still higher energies the populations decay with a time constant of 5 ps. This behavior is due to refilling processes that occur when “hot” electrons are scattered into states close to the CBM from higher energies. The population of states at higher energies, e.g., $E - E_{\text{cbm}} = -0.4 \text{ eV}$, decreases due to outscattering processes whereas the population of states at lower energies, e.g., $E - E_{\text{cbm}} \leq -1.0 \text{ eV}$, is refilled with these electrons. There is also the possibility of a weakening of the band bending by the space charge due to the photoexcited electrons.¹⁵ However, this mechanism will only make the refilling more pronounced when the conduction band bends downwards in the process of charge equilibration on a time scale of a few picoseconds after photoexcitation of the carriers.

Figure 2(b) shows the 2PPE measurements at the flat-band (011) surface that indicate fast electronic dynamics. However, the kinetic energies of the photoemitted electrons now correspond to electronic surface states in the fundamental gap. For delays of more than 1 ps these states all show a slowly decreasing electron population, in contrast to the result obtained for the (100) surface.

Figure 3 shows the dynamical spin polarization obtained from the spin-resolved dynamical 2PPE signals¹⁴ for electrons with definite kinetic energies $E - E_{\text{cbm}}^0 = -1.1 \text{ eV}$ and -1.0 eV from the GaAs (100) and (011) surfaces. Comparing the delayed rise of the dynamical spin polarization in Fig. 3 to the rise of the spin-integrated signals in Fig. 2, one notices that carriers emitted during the overlap of pump and probe pulses are mainly unpolarized because otherwise the spin polarization should reach its maximum at the same time as the spin-integrated signal. By fitting the polarization dynamics to an exponential decay for delay times $\tau > 10 \text{ ps}$, we obtain spin-relaxation times for states at the surface over the whole energy range of the band bending. For the (100) surface and energies $E - E_{\text{cbm}}^0 = -1.1 \text{ eV}$ and -1.0 eV , we obtain spin-relaxation times of $\tau_{\text{spin}} \approx 500 \text{ ps}$ and 150 ps , respec-

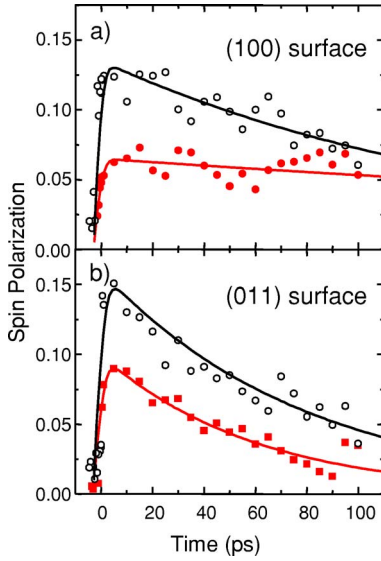


FIG. 3. (Color online) Dynamical spin polarization (dots) derived from 2PPE signal photoemitted from (a) the GaAs (100) surface and (b) the (011) surface, as well as corresponding exponential fits. The electron kinetic energies are $E - E_{\text{cbm}}^0 = -1.0$ eV (upper curves) and $E - E_{\text{cbm}}^0 = -1.1$ eV (lower curves).

tively. In the case of the (011) surface without band bending, we obtain from Fig. 3(b) at the same energies $E - E_{\text{cbm}}^0 = -1.1$ eV and -1.0 eV almost constant spin relaxation times of 60 ps and 70 ps, respectively. It should be stressed that the spin-resolved 2PPE method allows us to monitor the spin polarization up to more than 100 ps when the photoelectron yield, and thus the carrier density, is very small.

Figure 4 shows the spin-relaxation times extracted from the spin- and energy-resolved 2PPE measurements over a range of energies for both the GaAs (100) and (011) surfaces. For the GaAs (100) surface we observe an increase from about 60 ps to 1600 ps over an energy range of more than 0.3 eV, whereas the spin-relaxation time for the (011) surface is about 60 ps, independent of energy. The bulk spin

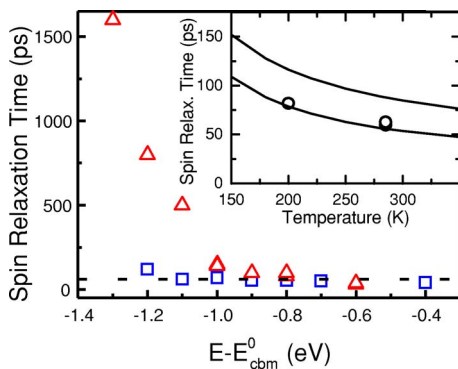


FIG. 4. (Color online) Spin relaxation times vs energy for the GaAs (100) surface (triangles) and (011) surface (squares). The dashed line indicates the bulk spin relaxation time at room temperature obtained from TRFR measurements. Inset: Temperature dependence of *bulk* spin relaxation time obtained from TRFR measurements (open circles) and calculations using the BAP mechanism for hole densities of 4 and $7 \times 10^{18} \text{ cm}^{-3}$ (upper and lower solid lines).

relaxation was measured on an identical sample by means of the time-resolved magneto-optical Faraday effect.^{16,17} The bulk spin-relaxation time was found to be 60 ps at room temperature regardless of the crystal orientation and is also shown in Fig. 4 as a guide to the eye. The spin-relaxation times for the (011) surface and at higher energies for the (100) surface are equal to the bulk value. In these cases there appear to be no additional contributions to electron spin-flip scattering that enhance the spin relaxation.

It remains to explain the different energy dependences for both surfaces in the light of earlier theoretical results that predict an increasing spin relaxation time at lower kinetic energies due to intrinsic properties of the BAP mechanism.¹⁹ To clarify this point we theoretically investigate the spin-relaxation time due to the BAP mechanism,³ which is expected to dominate in the present temperature and doping density range.¹⁸ The original analysis¹³ introduced an explicitly momentum dependent spin decay rate $1/(2\tau_{\text{BAP}}^s)$ in Born approximation that describes the spin-dependent population relaxation $\partial_t n_{s,k} = -1/(2\tau_{\text{BAP}}^s(k)) [n_{s,k} - f_{s,k}]$ with

$$\frac{1}{2\tau_{\text{BAP}}^s(k)} = \frac{2\pi}{\hbar} \sum_{\vec{q}, \vec{p}} \sum_{j, j'} |\langle j' s' | V_{\text{exc}}(\vec{q}) | s j \rangle|^2 n_{j, \vec{k}+\vec{q}} (1 - n_{j, \vec{p}+\vec{q}}) \times \delta(\epsilon_{j, \vec{k}+\vec{q}} + \epsilon_{s, k} - \epsilon_{-s, p} - \epsilon_{j', \vec{p}+\vec{q}}). \quad (1)$$

Here, $n_{s(j),k}$ are the momentum-dependent carrier distributions, s is the spin projection quantum number, and $j = \pm 3/2, \pm 1/2$ the hole angular momentum projection quantum number. The electron and hole energies are denoted by ϵ_s and ϵ_j , respectively. The interaction matrix element due to long-range and short-range exchange interaction $\langle j' s' | V_{\text{exc}}(\vec{q}) | s j \rangle$ is defined in Ref. 19. The electron equilibrium distribution, towards which the electron spin relaxes, is denoted by $f_{s,k}$. Using this relaxation time equation and taking into account that an electron that undergoes a spin-flip increases the number of electrons with opposite spin, one obtains for the case of unpolarized holes that the spin decay rates $1/(2\tau_{\text{BAP}}^s)$ are independent of the spin orientation s and consequently $\partial_t P_k(t) = -[\tau_{\text{BAP}}(k)]^{-1} P_k(t)$ as the dynamical equation for the momentum-dependent electron spin polarization P_k . Using this reasoning, the spin decay rate has been computed as a measure of the spin relaxation¹⁹ and was found to be strongly momentum dependent for both bulk and quantum well GaAs at $T=0$ K. Our explicit numerical evaluation of Eq. (1) without further approximations shows that this momentum dependence, which translates into an energy dependence, of the spin lifetime persists at room temperature. However, for low electron densities around room temperature as in the case of our experiments, the electronic distributions n_{sk} can be approximated by Maxwell-Boltzmann distributions so that $P_k(t)$ becomes momentum (energy) independent and the spin relaxation rate is given by the energy independent average of Eq. (1). This result has been checked against a numerical solution of the full Boltzmann equation for bulk GaAs including both spin-flip exchange scattering and spin-conserving direct Coulomb scattering similar to the approach in Ref. 20. The inset in Fig. 4 shows that the bulk results calculated in this way for the

range of hole densities of $4\text{--}7 \times 10^{18} \text{ cm}^{-3}$ are in good agreement with the Faraday effect experiments over a temperature range of more than 100 K, in which the BAP mechanism is expected to be the dominant spin-relaxation mechanism. Since the calculated spin relaxation due to the BAP mechanism in our experiments is energy independent, the energy dependence of the spin relaxation times in the band-bending region of the GaAs (100) surface can only be explained by a change of the material properties at the surface, which modifies the BAP scattering efficiency for electrons localized by the band-bending potential at the surface. This is most likely the reduced density of holes in the band-bending region since the holes are driven away from the surface. Using our calculations, we estimate that a reduction of the hole doping concentration of about one order of magnitude in the band-bending region is responsible for the long-lived spin polarization at the (100) surface. The above argument applies to low-energy electrons localized at the (100) surface; electrons at higher energies are not localized in the band-bending region and therefore show the same energy independent spin relaxation time as electrons at the (011) surface and in the bulk.

In summary, we have presented a study of spin-flip processes in the band-bending region of an interface between a *p*-doped semiconductor and a metal by means of spin and time-resolved 2PPE. This method is complementary to bulk sensitive Faraday rotation measurements, and yields the energy-resolved spin dynamics of electrons at surfaces. It is shown that the spin-relaxation time can exceed the carrier lifetime by an order of magnitude. Comparing these results to spin relaxation times in the bulk as obtained from our Faraday rotation measurements on identical samples as well as the numerical evaluation of the BAP spin-flip scattering rate, we do not find additional contributions for spin scattering at the (011) surface. For the (100) surface, the spin relaxation rate is decreased compared to the bulk value for electrons in the band-bending region at the surface due to the lower concentration of holes, which act as scattering partners for the spin-flip electron-hole exchange scattering.

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*Now at Dept. of Physical Chemistry, Chalmers University, Gothenburg, Sweden.

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