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Light emission from Er at the As-terminated Si(111) surface

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Erbium atoms at an arsenic-terminated Si(111) surface can be made to emit light at the 1.55 μm wavelength associated with an internal transition in the Er^{3+} ion. The As-terminated surface prepared under ultrahigh vacuum conditions has a surface recombination velocity of 50 cm s^{-1} and partially suppresses competing nonradiative recombination mechanisms. Following the deposition of Er, its characteristic light emission is observed only after oxygen reacts with the surface. The intensity of the light emitted by Er increases significantly upon cooling from 310 to 215 K. No light emission was observed from Er atoms deposited on 7×7 or H-terminated surfaces. © *2000 American Institute of Physics.* [S0003-6951(00)04140-1]

The use of Er as a light emitting impurity in Si has been motivated by potential device applications which take advantage of the fact that the energy of an internal transition in the Er^{3+} ion corresponds with the wavelength of minimum absorption of silica optical fibers.[1] In bulk Si the excitation of Er occurs by the transfer of energy from excess electrons and holes to the Er ion. Certain aspects of the atomic scale environment of optically active Er atoms have been determined by extended x-ray absorption fine structure measurements,[2,3] the study of the crystal-field splitting on photoluminescence spectra,[4] and by modifying the chemical environment of the Er with ion implantation of impurities.[5] The conclusion of these studies is that Er atoms must be coordinated with impurities, such as oxygen, to participate efficiently in the light emission process.

A more comprehensive understanding of the local atomic and electronic structure of the optically active Er and its environment will contribute to a deeper understanding of light emission processes for silicon based devices. Towards this end, we have discovered that Er ions at the As-terminated Si(111) surface emit 1.55 μm light in ways that are related to the behavior of Er in the bulk: optical activity is induced by oxidation of the Er doped surface. This observation makes Er and other optically active dopants susceptible to study by photoemission and scanning probe tools.

These experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with sources of As and Er. The sample was held so that both faces could be studied by low energy electron diffraction (LEED) and Auger electron spectroscopy. Minority carrier lifetime measurements were performed in UHV using an eddy-current based contactless photoconductivity decay method.[6] Excess carriers were excited for the lifetime measurement using up to 10 mW of 905 nm light. For optical spectroscopy, two laser diodes, with wavelengths centered near 800 and 900 nm, respectively, could be interchanged as sources of the 0.4 W pump beam. A spot 0.2×0.4 cm^2 was illuminated. The current to the laser diode was modulated to produce 50% duty cycle square pulses at 100 Hz for use in synchronous detection. Light emitted by the sample was collected by a lens,

dispersed by a monochromator, and sent to a liquid nitrogen cooled Ge detector.[7]

The 1 cm×2 cm samples were cleaved from 500 μm thick, (111) oriented, >1000 Ω cm resistivity, p-type wafers. Measurements performed with the sample immersed in concentrated HF indicated a lower limit of 700 μs for the bulk minority carrier lifetime.[8] Following chemical oxidation by the Shiraki process,[9] the samples were loaded into UHV. Resistive heating to 875 °C to evaporate the oxide layer produced the 7×7 LEED pattern on both sides of the sample. Bulk defects generated during heating resulted in a decrease in the bulk lifetime to 400 μs, as observed by measurements in HF after removing the sample from UHV.

The arsenic terminating layer was deposited by cooling the sample from 875 to 350 °C in a flux of As vapor from an effusion cell that was set to fill the chamber to a pressure of 10^{-5} Torr. Both sides of the sample then exhibited a sharp 1×1 LEED pattern that has been previously associated with As atoms residing near substitutional sites.[10] The As coverage was 0.96±0.05 ML (1 ML=7.83×10^{14} atoms cm^{-2}). Surface coverages of As and Er were measured using Rutherford backscattering spectrometry after removing the sample from UHV. Before termination with As, the minority carrier lifetime with the 7×7 surface was less than 15 μs, the minimum decay time measurable with our apparatus. A short lifetime is consistent with the high surface recombination velocity for the 7×7 surface reported in previous measurements.[11] With As-terminated surfaces, the minority carrier lifetime reached 255 μs. The corresponding surface recombination velocity was 50 cm s^{-1}, which is similar to previous results.[12] With the more intense pump beam used for light emission measurements, the surface recombination velocity was 500 cm s^{-1}. An Auger peak due to C was observed following As termination, with a Si LVV to C KLL ratio of 50:1.

Submonolayer amounts of Er were deposited on the surface from an Er foil spot welded to a Ta foil which was resistively heated to 900 °C. During Er deposition, the pressure rose briefly to 3×10^{-10} Torr. The addition of Er atoms to the As-terminated Si(111) surface produced an immediate drop in the intensity of band-gap light emission observed during luminescence measurements, due to a drop in the mi-

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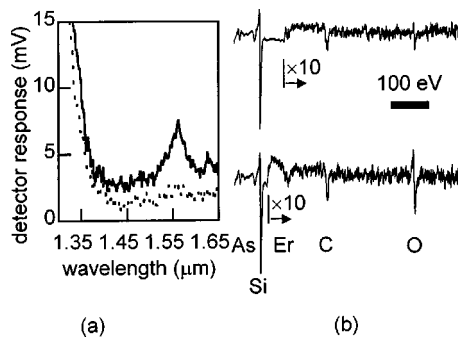a)Electronic mail: golovchenko@physics.harvard.edu

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FIG. 1. (a) Photoluminescence spectra 1 h (dashed) and 15 h (solid) after depositing 0.2 ML Er. The increase in intensity at short wavelengths indicates the onset of band-gap luminescence. (b) Auger electron spectra acquired in the dN/dE mode 0.4 h (top) and 26.5 h (bottom) after the Er deposition. Peaks due to As, Si, Er, C, and O are labeled.

FIG. 2. Fluorescence of Er_2O_3 (squares) and Er on As-terminated Si(111) (circles) vs pump laser wavelength: (a) Near 800 nm, (b) near 900 nm. In each plot, the signal from Er_2O_3 has been attenuated by the indicated factor.

nority carrier lifetime. Following the deposition of 0.2 ML Er, the intensity fell by a factor of 5. In the first few hours after depositing Er, there was no peak in the photoluminescence spectrum corresponding to light emitted by Er.

Within 15 h following the deposition of Er, a peak at 1.55 μm appeared in the photoluminescence spectrum. Figure 1(a) shows photoluminescence spectra taken 1 and 15 h after depositing 0.2 ML Er. Auger spectra in Fig. 1(b), taken 0.4 and 26.2 h after the deposition, show an increase over time in the oxygen KLL Auger peak at 505 eV. Following the initial increase of the oxygen peak, there was no additional oxidation of the surface in subsequent days. The appearance of oxygen was accompanied by a return of the band-gap light intensity to approximately half its value before the Er deposition. The limited oxidation of the surface following the deposition of Er suggests that the deposited Er atoms are oxidized by the residual gas. The base pressure in the chamber was 1×10^{-10} Torr. The emission of light at 1.55 μm only after the oxidation of Er at the surface is consistent with bulk studies in which efficient light emission requires the coordination of Er with impurities.[2] A similar oxidation of submonolayer Er films deposited on the Si(111) 7×7 surface has been previously observed in x-ray studies.[13]

By varying the wavelength of the pump beam while measuring the intensity of the luminescence at 1.55 μm, a distinction was made between direct absorption of the pump beam by Er compounds and absorption by the Si substrate followed by transfer of energy to Er at the surface. The intensity of the 1.55 μm fluorescence of Er on As-terminated Si and of Er_2O_3 powder are plotted in Fig. 2 as function of pump wavelength, which was tuned by varying the temperature of the laser diode in the range 0–30 °C. At each point, the intensity is normalized using the incident optical power. The fluorescence of Er_2O_3 powder shows a strong dependence on pump wavelength due to direct resonance excitation of Er. The intensity of the fluorescence from Er_2O_3 pumped near 800 nm is a factor of 400 greater than when pumped near 900 nm. Comparing the pump wavelengths with the level structure of Er in Er_2O_3 suggests that for the Er_2O_3 sample the excitation of the Er was strongest with the pump laser wavelength tuned to the $^4I_{15/2}-^4I_{9/2}$ transition near 800 nm.[14] A similar variation of the absorption cross section with wavelength is found for Er doped silica fibers.[15] In contrast, the fluorescence of the Er atoms on the As-
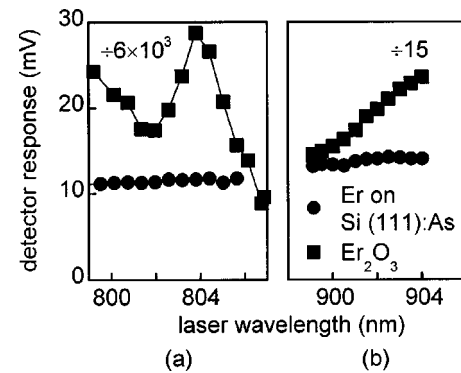
terminated surface was nearly independent of pump wavelength indicating that band-gap absorption by the Si substrate was responsible for the ultimate excitation of the Er atoms at the surface.

The surface recombination of electrons and holes resulting in light emission from Er competes with nonradiative recombination at surface defects. In analogy to the situation in which competing bulk processes are each characterized by a lifetime, the radiative and nonradiative surface recombination can each be assigned a surface recombination velocity. Using the absolute calibration of the detector system (1 mV peak signal$=5 \times 10^8$ photons cm^{-2} s^{-1} from the sample), an estimate of the relative magnitudes of the surface recombination velocities can be made.

An upper limit on the flux of excess carriers to the surface can be obtained by assuming that all of the electron-hole pairs created by absorption of the pump laser recombine at the surface. Assuming that each photon absorbed from the pump beam creates one pair of excess carriers, the flux of excess electrons to the surface is $\Phi_e = 2 \times 10^{19}$ cm^{-2} s^{-1}. In terms of the total surface recombination velocity ν_s, the concentration of electrons at the surface n_s is

$$n_s = \frac{\Phi_e}{\nu_s}. \tag{1}$$

The total surface recombination velocity, which is due almost entirely to nonradiative processes, is $\nu_s = 500$ cm s^{-1} when the sample is illuminated by the pump laser beam. The rate of radiative surface recombination is

$$\Phi_p = \nu_s^r n_s. \tag{2}$$

From Eqs. (1) and (2) we find that the ratio of the radiative surface recombination velocity to the total surface recombination velocity for our best sample, with 0.1 ML Er, is 10^{-8} at room temperature. Because the surface recombination velocity depends both on cross sections for electron and hole capture by defects and on the potential difference between the surface and the bulk of the sample,[16] it is not meaningful to use the present value for ν_s^r to determine a cross section for the light emission process. Room temperature quantum efficiencies of 10^{-4} for photoluminescence of Er in Si have been reported.[17] It will be an interesting challenge to identify and optimize the surface conditions necessary to obtain similar or superior results from Er at solid surfaces.
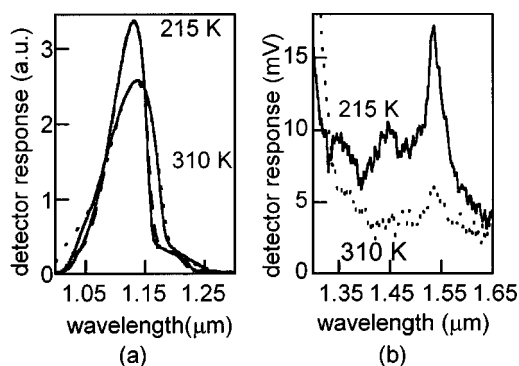
FIG. 3. (a) Band-gap light emission with and without cooling (solid lines). Fits to the spectra (dashed lines) give sample temperatures of 310 K without cooling and 215 K with cooling. (b) Increase in light emission from Er atoms at As-terminated Si surface upon cooling from 310 K (dashed line) to 215 K (solid line).

Cooling the sample through a Cu braid connected to a liquid nitrogen reservoir allowed the temperature dependence of the light emission from the Er atoms at the surface to be studied at temperatures from 215 to 310 K. The temperature dependence of the band-gap luminescence was used to measure the sample temperature by comparing the observed spectrum with one predicted using the van Roosbroeck–Schockley relation.[18] Agreement between theory and experiment is extremely good, as demonstrated in Fig. 3(a). Figure 3(b) shows the increase in the intensity of the peak at 1.55 μm upon cooling from 310 to 215 K, for a sample with 0.2 ML Er. A similar increase in intensity upon cooling observed for Er in bulk Si was attributed to a reduction in the thermally activated deexcitation of the Er ion.[19] In those studies, the intensity of the Er luminescence above 100 K was proportional to $\exp(E/kT)$, where $E \approx 0.15$ eV was the effective activation energy for the return of carriers from Er related traps to levels in the Si bands.[19] For our measurements, the increase in intensity upon cooling by a factor of 3.7 observed in Fig. 3(b), after subtracting the background, gives $E \approx 0.08$ eV. The cause of the difference between the present result and the previously reported value of E may include effects of changes in the total surface recombination velocity with temperature, and/or a difference in the energy of the Er-related defect level through which an Er ion is excited.

No light emission was observed from Er on H-terminated surfaces loaded into UHV after wet etching.[20] Although H-terminated samples exhibited a low surface recombination velocity before the deposition of Er, there was no recovery of the lifetime in the hours following the Er deposition in contrast to As-terminated Si. No light emission from Er was detected for Er deposited on 7×7 or chemically oxidized surfaces, which can be attributed in part to the high surface recombination velocities associated with these surface preparations. Light emission from Er atoms on the As-terminated Si(111) surface also ceased upon removing the sample from UHV.

Future experiments taking advantage of the tools of surface science will further the study of the mechanisms by which energy is transferred from excited carriers in Si to Er atoms at the surface. The issues to be resolved for a complete understanding of surface light emission include the effects of surface potential, the origins of nonradiative surface recombination, and the detailed environment of the Er atoms. It is our hope that by optimizing the conditions for Er light emission at surfaces these regions can ultimately be incorporated in bulk devices via epitaxial growth techniques.[21]

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