Reconstruction-dependent electron-hole recombination on GaAs(001) surfaces studied by using near-surface quantum wells

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Using an ultrahigh-vacuum photoluminescence system, electron-hole recombination on clean reconstructed GaAs(001) surfaces is characterized by measuring photoluminescence spectra of near-surface quantum wells. The luminescence from the quantum well with an As-rich (2×4) surface is stronger than that with a Ga-rich (4×6) surface, showing that the surface recombination is faster with (4×6) than with (2×4).

Electron-hole surface recombination plays an important role both in semiconductor physics and device performance. Despite this importance, the origin of the recombination, the surface state, has not yet been clarified as well as that causing surface Fermi-level pinning. One of the reasons is that the surfaces on which the electron-hole recombination has been studied are not well-defined, regardless of the type of samples. In many cases, the surfaces were exposed to the atmosphere and the atomic structures are very complicated.

One solution to this problem is to study the surface recombination on well-defined clean surfaces. The surfaces we report in this paper are clean reconstructed GaAs(001) surfaces, whose atomic structures have been recently clarified by modern structural analysis methods like scanning tunneling microscopy[1–9] (STM) and theoretical calculations.[10–14] By using an ultrahigh-vacuum (UHV) photoluminescence (PL) system, electron-hole recombination on these reconstructed clean surfaces has been studied and the origins of the recombination are discussed based on structural models of these surfaces.

For this study, the PL spectra of near-surface quantum wells (NSQW's) were measured with a UHV-PL system. This method was first proposed by Moison *et al.*[15] In the method, the magnitude of the interaction between a NSQW and a surface can be evaluated from the change in the PL spectrum as a function of the spacing between the NSQW and the surface. Results with etched surfaces,[16,17] hydrogen treated surfaces,[18] Si-inserted interfaces,[19] and time-resolved PL measurements[20] have been reported, but all these reports are concerned with the air-exposed surface (except for Moison's report).

The surface reconstructions used in this study are As-rich $(2\times4)/c(2\times8)$ [referred to as simply (2×4) hereafter], which is a most important surface for device fabrication by MBE growth, and Ga-rich (4×6). The former has an As dimer-vacancy row structure, as has been established by recent STM observations.[1,2,4,6–8] *Ab initio* calculation indicates that no surface state is formed definitely in the fundamental band gap for an ideal (2×4) surface.[14] The detailed atomic structure of the (4×6) surface has recently been reported.[9] There is no report on the detailed band structures for these surfaces, but it is expected that the surface energy-level alignment of (4×6) is different from (2×4) and these two surfaces show different surface recombination velocities. The dependence of surface recombination on surface reconstruction has been reported by Sandroff *et al.*,[21] but they obtained reconstructed surfaces by annealing As-decapped samples, in an ultrahigh vacuum, which were once exposed to air after MBE growth. The uniformity of the surface reconstructions prepared by this method is lower than that by an *in situ* method, and it is not easy to control the surface stoichiometry, as has been discussed in some reports.[1,6,22,23] Disorder in surface reconstruction caused by this method functions as surface states, which can be the origin of surface recombination,[24,25] and an *in situ* sample preparation is necessary especially for characterizing surface recombinations. Therefore, in the present paper, we used well-prepared reconstructed clean surfaces that were directly transferred through UHV from the MBE chamber to a PL chamber. From the results, it is quantitatively clarified that the recombination velocity is faster with Ga-rich (4×6) than As-rich (2×4) surfaces.

The PL measurements were performed with the samples in an UHV chamber whose pressure was kept lower than 4×10^{-10} torr. This chamber was directly connected through UHV to an MBE growth chamber. Samples can be transferred from the MBE to the PL chamber without contaminating the surfaces, and then they can be cooled by a liquid nitrogen cryogenic mechanism down to 140 K. Reflection high-energy electron diffraction (RHEED) observation can also be performed for structural study at low temperatures with the same sample arrangement as for the PL measurements. The sample was excited by an argon laser with a wavelength of 488 nm, which excites not only the quantum well (QW) but also the $Al_xGa_{1-x}As$ barrier layers. The laser beam was focused on a 100-μm square on the sample. The growth rates of GaAs and $Al_xGa_{1-x}As$ are different over the sample surface, thereby causing a change in the PL spectrum from the QW. This change obscures the true dependence of NSQW intensity on the surface reconstruction. To avoid this difficulty, the PL measurement was performed at a fixed point on the samples with an accuracy of 1 mm.

The fabricated QW structures are shown in Fig. 1. The substrates, undoped semiinsulating GaAs(001) wafers, were processed according to a standard procedure before loading into the chamber. Two QW's were grown on the substrate. One, written as Ref-QW in the figure, is for PL intensity calibration and the other, NSQW, is for characterizing the surface recombination. By changing the $Al_{0.3}Ga_{0.7}As$ top barrier layer thickness (d in the figure), the interaction between the NSQW and the surface can be controlled. The surface of

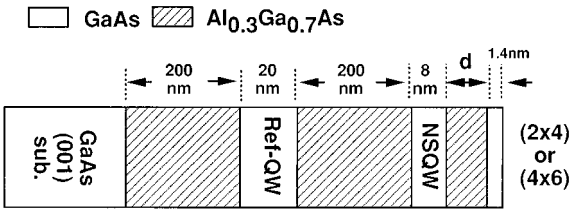

FIG. 1. Fabricated sample structures.

the sample was covered by 5 ML of GaAs to obtain a well-established surface structure of GaAs because the surface structure of $Al_xGa_{1-x}As$ has not yet been studied in detail. The GaAs surface layer is thick enough to ensure surface properties of GaAs and thin enough to avoid an additional quantum level confined in it. The vacuum/GaAs/$Al_xGa_{1-x}As$ structure forms an asymmetric quantum well but there is no quantum level in it because the vacuum barrier is sufficiently high.[26] A MBE machine equipped with a valved cracker cell for the As source was used for sample fabrication. Using the cell, the background As pressure can be reduced quickly. This is useful for controlling the surface stoichiometry and preparing a definitely reconstructed surface after the growth. The (2×4) surfaces were prepared as follows. The sample was annealed under As flux for 3 min, and then it was cooled and the As valve was closed. The detailed procedure was optimized to obtain the most uniform (2×4)-β structures[7,8,27] confirmed by RHEED observation. The (4×6) surfaces were prepared by depositing 1 ML of Ga atoms on the (2×4) surface at 500 °C.

RHEED patterns obtained at 140 K just before the PL measurements are shown in Fig. 2. Clear (2×4) and (4×6) structures were confirmed even after cooling the samples. No significant structural change was confirmed from the patterns obtained at room temperatures. The fourfold pattern of the (2×4) surface shows sharp peaks both on fractional- and integer-order lines along the zeroth-order Laue zone. This indicates that the surface is atomically flat and the fourfold periodicity is highly coherent. The twofold pattern of (2×4) is a bit disordered probably due to the mixture of (2×4) and

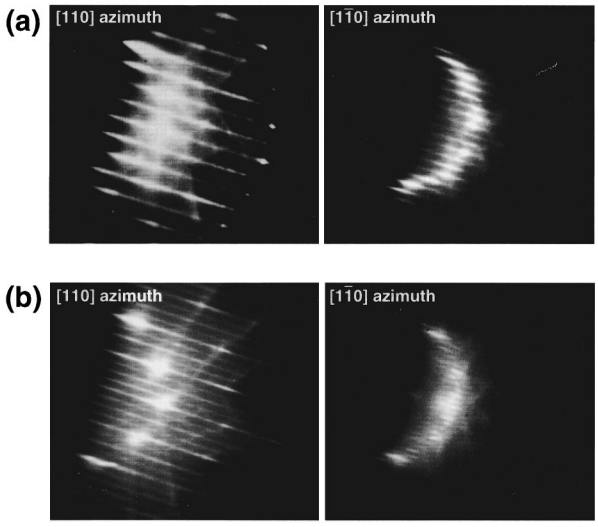

FIG. 2. RHEED pattern obtained at 140 K before PL measurements: (a) (2×4) surface and (b) (4×6) surface.

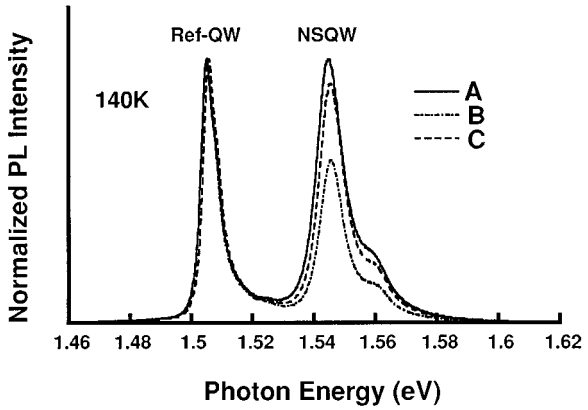

FIG. 3. PL spectra of a fabricated sample with a top $Al_xGa_{1-x}As$ barrier layer thickness of 10 nm. The sample temperature is 140 K and the excitation power is 7 mW. Sample *A* has (2×4) reconstruction transferred just after the MBE growth. Sample *B* has (4×6) reconstruction prepared by depositing 1 ML of Ga on sample *A*. Sample *C* has (2×4) reconstruction prepared by annealing sample *B* in As pressure.

c(2×8) phases. The (4×6) pattern shows sharp peaks on integer lines but no sharp peak on fractional-order lines both on fourfold and sixfold lines. This indicates that the (4×6) surface is also atomically flat, but there are many phase boundaries, i.e., disorder, in the periodic structures.

PL spectra of the quantum well structures for $d=10$ nm are shown in Fig. 3. We measured PL spectra of the structure with three different surfaces. Sample *A* has a (2×4) reconstruction prepared just after the MBE growth. Sample *B* has a (4×6) reconstruction prepared by Ga deposition on sample *A* at 500 °C, and sample *C* was prepared by exposing sample *B* in As flux, and it has (2×4) reconstruction. The PL intensity (vertical axis) was normalized to equalize the intensity of the Ref-QW's. The luminescence from the NSQW of sample *B* is weaker than those of *A* and *C*, showing that the surface recombination is faster with (4×6) than with (2×4). The intensity from the NSQW is almost the same between *C* and *A*. From this results and those by RHEED observation, we believe that there is no significant contamination of the sample surfaces during the sample transfer and the cooling process. The observed PL intensity difference is, therefore, due to the native dependence of recombination velocity on the surface structure.

The relative integrated PL peak intensity, i.e., (NSQW integrated peak intensity)/(Ref-QW integrated peak intensity) is shown in Fig. 4, as a function of the top $Al_xGa_{1-x}As$ layer thickness *d*. The intensity reduced by decreasing *d* as reported by Moison *et al.*[15] The intensity was more rapidly reduced for (4×6) than that with (2×4). As has been mentioned already, the excitation was performed by a 488-nm line of Ar laser, which excites both quantum wells and barrier layers. Therefore, the reduced luminescence from NSQW has two origins. One is the recombination of electron-hole pairs diffused into the surface from the two $Al_xGa_{1-x}As$ barrier layers. The other is the recombination of electrons (or holes) tunneled from a quantum well after being trapped by the well. It is very difficult to distinguish these two processes but, at least, the reduced PL intensity from the NSQW directly indicates increased surface recombination.

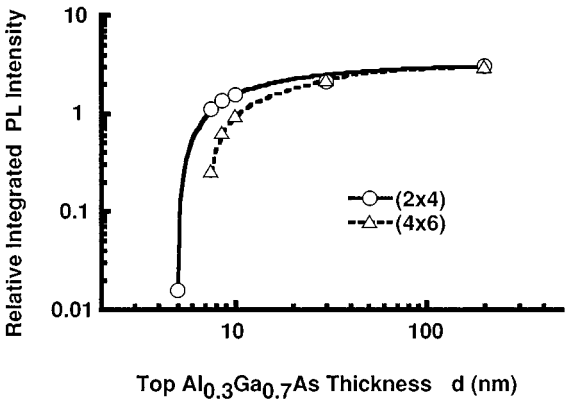

FIG. 4. Normalized integrated PL intensity of NSQW versus surface $Al_xGa_{1-x}As$ barrier thickness. The lines are guides for the eyes.

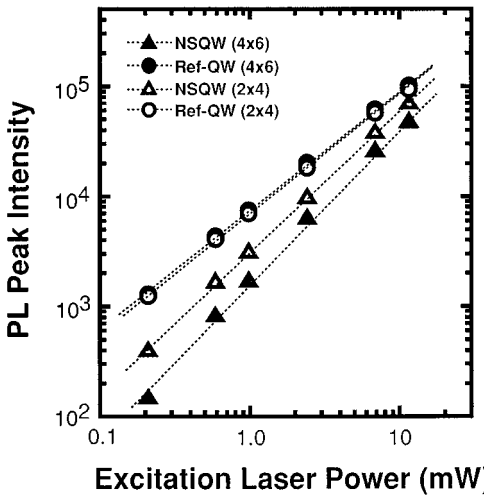

FIG. 5. Excitation power dependences of PL peak intensity of Ref-QW's and NSQW's for (2×4) and (4×6) surfaces. The $Al_xGa_{1-x}As$ barrier layer thickness is 8.6 nm.

Moison *et al.* have also reported a redshift of more than 10 meV for thinner $Al_xGa_{1-x}As$ barriers. In our measurements with the (2×4) surface, the peak position of the NSQW is constant with an error of less than 1 meV. This discrepancy may be due to the difference in the surface reconstruction [they used a $c(4\times4)$ surface] or the presence of a surface GaAs layer. The peak position of the NSQW with the (4×6) surface was redshifted from that with (2×4), but the shift is only 1.5 meV for d of 7.5 nm, which is much smaller than that reported in Ref. 15.

The excitation power dependences of the PL peak intensity of NSQW and Ref-QW's are shown in Fig. 5. With the Ref-QW, the dependence is nearly linear. If the dependence is fitted by a power law, the exponent is 1.08 for the (2×4) surface and 1.09 for the (4×6) surface and, on the other hand, 1.28 for (2×4) and 1.43 for (4×6).

As mentioned before, the (4×6) surface is more disordered than the (2×4) surface. One possible explanation for the faster surface recombination with (4×6) is the disorder in the surface structures. Two kinds of surface structure of the (4×6) reconstruction were observed by STM observation. One is "genuine" (4×6) with periodically aligned Ga clusters along Ga-dimer vacancy rows. The other is "pseudo" (4×6) which is a mixed phase of (2×6) and (4×2) [or "genuine" (4×6)].[9] It is not clear which is our (4×6), but the recombination is expected to be faster with (4×6) in both cases.

For "genuine" (4×6), the Ga clusters cause high density of surface states because the energy-level structure of a Ga cluster is probably metallic. The wave function can penetrate into the semiconductor and form a high density of surface states as for metal induced gap states of metal-semiconductor junctions.[28,29] Even if the energy-level structure is not metallic, a high density of half-filled dangling bonds causes surface states, which can function as nonradiative recombination centers. For "pseudo" (4×6), the phase boundary of differently reconstructed domains does not satisfy an electron counting rule, and it forms surface states. Independent of the detailed atomic structure, the fact that the surface structure is disordered is sufficient to explain the high density of surface states because the disorder disturbs the surface band structure, and discrete levels are formed in the band gap.

In conclusion, PL spectra were obtained for NSQW structures with clean reconstructed surfaces of (2×4) and (4×6). The luminescence from the NSQW is weaker with (4×6) than with (2×4). This result clearly indicates that the surface recombination velocity is faster for the Ga-rich surface than for the As-rich surfaces.

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