B－5－3 Influence of Ambient Gas on the PL Intensity from InP and GaAs

H. Nagai, Y. Noguchi and Y. Mizushima
Musashino Electrical Communication Laboratory
Nippon Telegraph and Telephone Public Corporation, Musashino, Tokyo

Reversible change of photoluminescence(PL) intensity with change of gaseous ambients(N_2,Ar,H_2,O_2,H_2O and vacuum) from InP crystal surface, and irreversible change of PL from GaAs cleaved surface when exposed to oxygen were observed at room temperature. These phenomena imply that adsorbed gases can be exchanged reversibly on InP surface, and the surface recombination velocity changes reversibly with the adsorbed gas species. On the other hand, oxidation proceeds rapidly and irreversibly on GaAs cleaved surfaces. In addition, three types of characteristic behaviours of PL intensity response were found for InP crystal surface according to various surface preparations and measuring ambients.

For the PL measurement in various ambients, sample crystal was set in a fused quartz tube which has a flat window surface. O_2, N_2, H_2 or Ar gas of 1 atm was led into the quartz tube. The PL was excited by the 6328 Å emission from a He-Ne laser with an excitation density of 2 W/cm^2. The PL intensity at the peak of the intrinsic recombination wavelength was detected by a photomultiplier combined with a grating monochrometer of 100 Å resolution.

Figure 1 shows a reversible PL intensity response from n-type InP cleaved surface with change of the gaseous species($N_2 \leftrightarrow O_2$). The PL intensity changes reversibly by alternation of N_2 and O_2 for many times. Instead of N_2, H_2 or Ar has nearly the same effect. Figure 2 shows the result of the same experiment performed on GaAs (110) cleaved surface. In this case, an irreversible change takes place. Figure 1 and 2 show the difference of surface properties of InP and GaAs. The fresh GaAs surface is apparently oxidized quickly when exposed to O_2 or air. On the contrary, the fresh InP surface seems to be oxidized very slowly. Assuming that the PL intensity change originates from the change of the surface recombination velocity, change of the surface recombination velocity is estimated as 1～2 orders of magnitude.

PL intensity response is also found for InP and GaAs crystal surfaces relating to the humidity change of the ambient gases. Figure 3 shows the example for n-type InP cleaved surface. The ambient gases are dry N_2, wet N_2(17mmH_g H_2O), dry O_2 and wet O_2. H_2O vapor in each gas makes the PL intensity strong comparing to the dry gas, and PL response is reversible in these ambients. For GaAs, H_2O vapor has the analogous effect, though the PL decreases slowly in the wet gas and finally becomes insensitive to the gas change. The surface recombination

velocity is affected strongly by H_2O molecule adsorption and desorption.

For InP, 3 types of behaviours of PL response were found according to various surface preparations and measuring ambients. Figure 4 shows the examples. Gradual increase of PL occurs on the surface etched by methanol-Br_2 solution in all the examined gases. Gradual decrease appears on the surface treated by HNO_3,HF,HCl and H_3PO_4, and in the O_2 containing gases. These tendencies can be repeated reversibly. The adsorbed etchant ions, remaining on the surface even after the rinse, should be the cause of these phenomena. The reversibility of Fig. 1 and 3 can be seen on these surfaces. PL from the surface treated by $AgNO_3$ and $CuSO_4$ solution is fixed at a low level, and quite insensitive to all the gases. Ag or Cu ions strongly obstruct adsorption of the gas molecules. PL response of Fig. 4 can not be seen for GaAs. For InP, the present phenomena of Fig.1,3 and 4 are remarkable in n-type crystal of high carrier concentration. For p-type, these are not distinct.

The facts reported here imply that the monomolecular adsorbed state without chemical binding is unambiguously detected. Reversible adsorption with only several kcal/mol is firstly found to affect the surface recombination velocity. PL is found as a sensitive measure of the adsorption-enhanced surface state. It is also suggested that there is a possibility to get the cleaved surface without recombination by properly protecting the surface from oxidation in GaAs devices. For InP devices, it will become simpler because of the weak oxidation velocity.

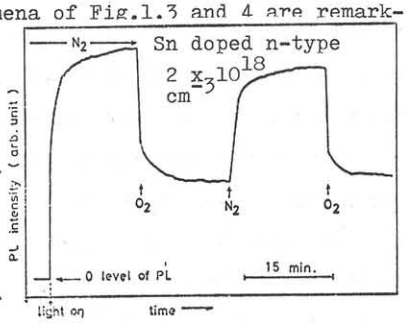

Fig. 1 Reversible PL response from InP (110) surface(cleaved in air).

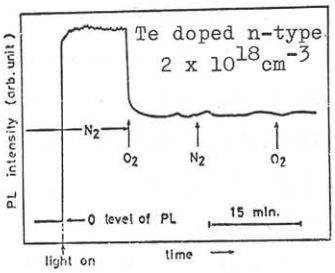

Fig. 2 Irreversible PL response from GaAs (110) surface(cleaved in N_2)

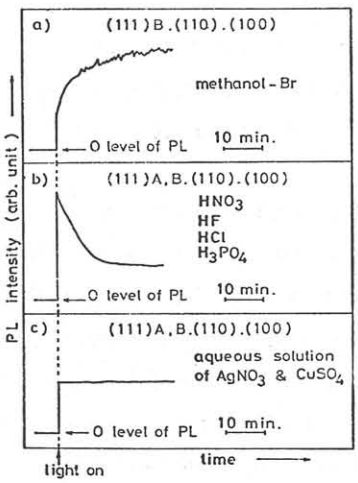

Fig. 4 Three types of PL response measured in air according to the surface preparation. Crystal plane is (100). Sn doped n-type InP, 2 x $10^{18}cm^{-3}$.

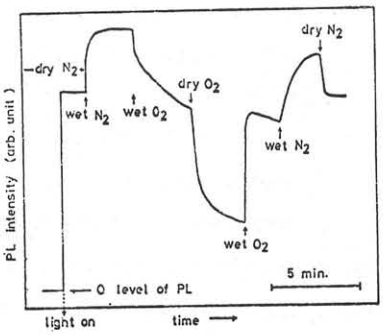

Fig. 3 Reversible PL response from the InP (110) surface (cleaved in air) with the humidity change. Sn doped n-type, 2 x $10^{18}cm^{-3}$.