Ion relaxation and hydrogen LVM in H-irradiated GaAsN

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Abstract

First-principles calculations show that the hydrogen configurations in GaAsN depend on how hydrogen is introduced into the sample. Since proton and neutral H have different ground states, the proton injected into the sample by H-irradiation follows a unique energy pathway to form a charged dihydride, instead of the charge-neutral H\textsubscript{2}\textsuperscript{*} monohydride. The subsequent charge neutralization causes the spontaneous canting of the dihydrides. The resulting canted N–2H structure explains the recent puzzling IR observation, the recoveries of the GaAs band gap and lattice parameter, and the dihydride symmetry determined by the XANES experiment. It may also have broad implications for ion implantation studies in other solids.

PACS: 61.72.Vv; 63.20.Pw; 61.72.Ji; 61.72.Bb

Keywords: Ion implantation; Dilute III–V nitrides; Hydrogen; IR modes

1. Introduction

Large size-mismatched dilute alloys such as GaAsN [1] and ZnSeO \cite{2,3} are promising alloy semiconductors with unique physical properties. For example, with only an atomic percent of N incorporated into GaAs, the band gap decreases by several hundred meV \cite{4}. On the other hand, H irradiation causes a nearly full recovery of the GaAs band gap \cite{5} and lattice parameter \cite{5} from those of GaAsN. The formed H complexes after H irradiation should be charge neutral due to their large concentration (>10\textsuperscript{20} cm\textsuperscript{-3}). First-principles total energy calculations suggested that the lowest-energy charge-neutral H complex is the \(\text{x-H}_2\text{N}\) complex with characteristic Ga–H and N–H monohydride bonds (Fig. 1a), and that this complex can explain the above experimental observations \cite{6,7}. However, a recent infrared experiment \cite{8} on H-irradiated samples did not observe any Ga–H modes. Instead, two N–H stretch modes were observed at 3195 and 2967 cm\textsuperscript{-1}, as shown in Table 1. Hence, both modes here belong to the N–H bonds. In D-irradiated samples, the two stretch modes shift to 2216 and 2376 cm\textsuperscript{-1}, respectively. In H/D co-irradiated samples, however, two additional D-stretch modes, at 2221 and 2366 cm\textsuperscript{-1} (see Fig. 2a), and one additional H-stretch mode, were observed. A second H mode is also expected, but was not observed, which was due possibly to contamination. The observation of the two (instead of one) additional D modes indicates that the H complexes must contain two inequivalent H atoms strongly coupled to each other. A recent XANES study \cite{9} further reveals that the symmetry of the 2 H complexes should be C\textsubscript{2v}-like, thus further undermining the validity of the C\textsubscript{3v}-based H\textsubscript{2}\textsuperscript{*} model.

The disagreement between theory and experiment on H configurations in GaAsN suggests that the observed H-complex may not be the ground-state configuration. During H-irradiation, the equilibrium between the injected protons and the electron reservoir of energy \(E_F\) is not maintained. Therefore, one cannot assume that protons will take the theoretically predicted ground-state structure for neutral H.

In contrast to the conventional view of H irradiation as simply another convenient mean to enhance H concentration [H] in the solid, in this paper, we will show that the final H configurations can be altered by how the H is