Native-nitridation of Semiconductor Surfaces at 20K : NH_3 on GaAs, InP and Si

Jae Myung Seo, Ki-Jung Kim, Myung-Hwan Ann and Chan Park
Department of Physics, Jeonbuk National University

Introduction

Up to now it is not so much successful to form a Metal-Insulator-Semiconductor Field Effect Transistor (MISFET) based upom Ⅲ-Ⅴ semiconductors. Instability of anions of Ⅲ-Ⅴ compound semiconductor under high temperature processing limited formation of the insulting layer on Ⅲ-Ⅴ semiconductor surfaces. Therefore it is the major goal to form a better interface between the semiconductor and insulating layer in order to reduce scattering by defects and preserve carrier concentration in the inversion layer. Since the external formation of insulating layer (i.e., not using the substrate-semiconductor) should have defects like grain-bondary, it is important to form a native insulating layer without severe deformation of the substrate. In this paper we will present the successful result of native-nitridation on Ⅲ-Ⅴ semiconductor as well as Si sufraces using condensed NH_3 on semiconductor followed by illumination of synchrotron white light.

Experimental

Nitride has been formed under ultrahigh (UHV) condition using condensed NH_3 on cleaved semiconductors (GaAs, InP and Si) through illumination of synchrotron white light. The Angle-Integrated photoemission spectroscopy was used in order to identify the reaction product and the condensed gas molecules. After semiconductor posts were cleaved under UHV (3×10^{-11} Torr) to produce mirror-like surfaces, the samples were cooled to 20K using a closed-cycle He-refrigerator. As the temperature of NH_3-condensation is far above 20K, the amount of condensed NH_3 is controlled by the leak pressure and time, assuming the sticking coefficient of NH_3 on semiconductors is near 1. Prior to NH_3, N_2 was tried but failed to break N_2 through illumination. Even for NH_3, the reaction by illumination of monochromatic X-ray was not proceeded. Hence the unmonochromatized white light (2-1500eV : Zero Order) was finally illuminated and nitrude were detected from the surfaces. In order to determine chemical shifts, the core-level spectra such as In 4d, P 2p, As 3d, Ga 3d, and Si 2p were analyzed with a least squares minimization routine that made it possible to decompose the spectra into components and to deterime the intensities of those components. Valence bands were also obtained to make sure of molecular condensation and hybridation between the substrate and the condensed components.

Result and Discussion

From the valence band N-lone pair orbital and $(N\text{-}H)_3$ orbital were identified after 1L of NH_3 exposure at 20K. After Zero Order light (Z.O.) was illuminated, N-H orbital intensity was reduced and the peaks due to orbitals between N and the substrate atom. At the same time the core-level chemical shift were also detected. For the repeated NH_3-exposure and Z.O. illumination, the reaction product increased. The summarized reaction products what we have formed and their chemical shifts are as follows :

Semiconductor	Reaction products	Chemical shift
InP[1]	P_3N_5	- 3.6 eV
	In N	- 0.4 eV
GaAs[2]	Ga N	- 0.7 eV
	As N	- 2.0 eV
	As N_x	- 3.3 eV
Si[3]	Si_3N_4	- 2.5 eV

It is remarkable to find AsN with chemical shift "-3.3 eV" relative to bulk since AsN is very unstable and never reported before. The attenuation and the intensities are varied depending upon the elements. Most of them are expected from heat of formation (Si_3N_4 : -177.7 Kcal/mole, GaN : -26.4, AsN : +46.9, InN : -4.2, P_3N_5 : -71.4). Two remarks must be pointed out here : (a) Heat of formation of GaAs and InP are -17.0 and -21.2 Kcal /mole, respectively. Even if the heat of formation of AsN and InN are higher than substrate, the nitridation using condensed phase made it possible to form such less unstable phases, AsN and InN. This is mainly due to strong kinetic constraint of components at 20K. (b) As-nitride like phase exist in two different local chemical bondings. Higher chemical-shift phase has not been reported and is due to also strong kinetic constraint of components at 20K. Therefore it is one of the most interesting points in this study whether it can be stable even at 300K.

Conclusions

Native-nitride can be formed at 20K using NH_3 and illumination of synchrotron white light. The novel phases of nitride at 20K could be formed due to strong kinetic constraints. It can be deduced that the novel phases can be formed if we provide the strongly constrained environment.

(1) Y.H.Jeong, J.H.Lee, Y.H.Bae, and Y.T.Hong, Appl. Phys. Lett. 57, 2680 (1990).
(2) P. Friedel, J.-P.Landesman, P.Boher, and J.Schneider, J. Vac. Sci. Technol. B5, 1129 (1987).
(3) C. Maillot, H.Reulet, and G.Dufour, J.Vac.Sci.Technol. B2, 316 (1984).