

## A New Surface Passivation of GaAs Using CVD —Atomic Layer Passivation—

Yoshinori WADA, Yoichi MADA, and Kazumi WADA

NTT LSI Laboratories  
3-1 Morinosato Wakamiya, Atsugi-shi, Kanagawa 243-01, Japan.

A new passivation concept for GaAs is proposed based on CVD experiments. Using tri-methyl-indium and phosphine, an ultra-thin (about 1 nm) layer is deposited on the GaAs surface. A remarkable enhancement of photoluminescence from the surface is observed that is about ten times larger than the photoluminescence from a non-treated surface. This indicates that the GaAs surface can be passivated by the ultra-thin layer, which we call "Atomic Layer Passivation (ALP)". A wide energy gap is essential for the ultra-thin layer and compressive strain plays an important role in the passivation.

### 1. INTRODUCTION

Treatment of GaAs surfaces by sulfur (S) atoms has brought about a remarkable reduction in surface recombination and the surface state densities.<sup>1)</sup> The mechanism of this treatment has been interpreted as the termination of dangling bonds at the GaAs surfaces with the group VI atoms<sup>2)</sup>, which we refer to as the bond termination picture. Recently, a group V element phosphorus (P) treatment using PH<sub>3</sub> plasma was also reported to reduce surface state densities,<sup>3)</sup> but this treatment seems less effective for bond termination. This suggests the existence of another picture.

A problem may arise also from the device applications because of the weak adhesion (van der Waals interaction) of the treated surface.

The purpose of this paper is to demonstrate GaAs surface passivation utilizing an ultra-thin semiconductor layer and to propose a new passivation concept based on energy band considerations. The ultra-thin passivation layer studied in this paper is an InP-related compound grown on the GaAs surface by chemical vapor deposition (CVD) technology. This process successfully provides the various treatments using VI, V and III atoms without damaging the surface.

### 2. EXPERIMENTAL

Mirror polished Si doped HB grown (100) GaAs wafers ( $n = 10^{17} \text{ cm}^{-3}$ ) were used. The wafers were, first of all, chemically etched, then placed in a CVD reactor. In

the reactor they were thermally cleaned and then treated in PH<sub>3</sub> with H<sub>2</sub> in a laminar flow condition. A very small amount of tri-methyl-indium (TMI) was supplied in the treatment. A CVD treatment using H<sub>2</sub>S was also carried out. The treatment temperature ranged from 400°C to 650°C.

An evaluation of the passivated surface properties was carried out by photoluminescence (PL) measurement because it is a nondestructive method that measures surface recombination without changing surface conditions. We confirmed that the PL intensity of the GaAs wafers used in this study varies only about 0.95 times the PL intensity of the as-etched wafer, even when the GaAs wafers received heat treatment under arsenic (AsH<sub>3</sub>) pressure in the above temperature range.

The treated GaAs surfaces were also analyzed using Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS). All of these analyses were undertaken on samples exposed to the atmosphere after the treatments.

### 3. RESULTS AND DISCUSSION

#### 3.1 TMI + PH<sub>3</sub> Treatment and H<sub>2</sub>S Treatment

A remarkable nearly 10-fold PL enhancement was observed on the TMI+PH<sub>3</sub> treated surface immediately after the CVD treatment (0 h), which is shown by curve A in Fig.1. Here, TMI was supplied to form a few atomic layers of an InP-related compound whose thickness was less than the critical layer thickness<sup>4)</sup> of the dislocation generation due to lattice mismatch. This PL

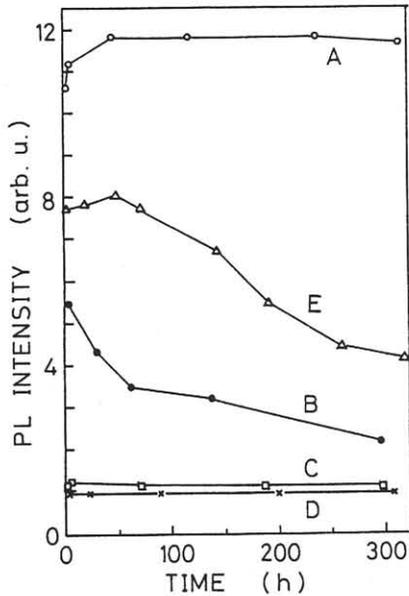


Fig.1 Photoluminescence intensities and their variations in time. The intensity at the GaAs band edge is measured. The values of the PL intensities are normalized by the values of as-etched GaAs samples.

enhancement indicates that the GaAs surface can be passivated by the ultra-thin compound semiconductor layer. Moreover, this passivated surface did not degrade much in PL intensity, as shown by curve A, even though it was exposed to the atmosphere.

Sulfur (S) treatment using  $H_2S$  is shown by curve B in Fig.1. The PL enhancement at 0 h was about 5, which is half the enhancement described for the InP-related compound. Furthermore, the S treated surface shows gradual decrease in the PL intensity.

This indicates that the deposition of an ultra-thin compound semiconductor layer could be another breakthrough in surface passivation technology.

It is notable that S treatment using  $(NH_4)_2S_x$  solution showed at most a 3.5-fold PL enhancement in our experimental condition, which clarifies the usefulness of this CVD process.

### 3.2 Structure of the InP-related layer

The auger electron depth profile of the InP-related layer is shown in Fig.2. The sputtering rate was about 0.5 nm/min. The signals of carbon (C) and oxygen (O) decrease rapidly with sputtering time; however, the In and P signals remain longer. In contrast with these four signals, Ga and As signals saturate at about 2 min.

Arsenic was not present on the surface since no arsenic oxides were found in the XPS data. Thus, the As and Ga signals detected at 0 min (surface) are mainly that from the substrate. Considering the electron escape depth and the AES data shown in

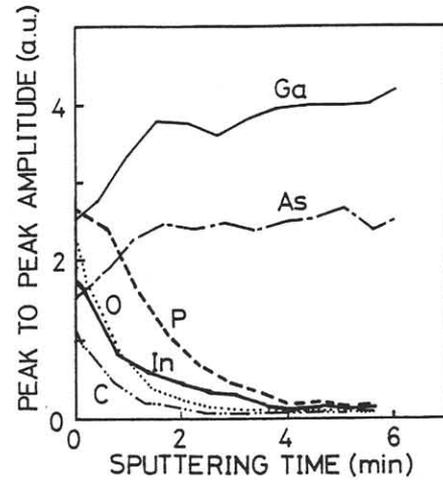


Fig.2 Depth profile of a TMI +  $PH_3$  treated sample.

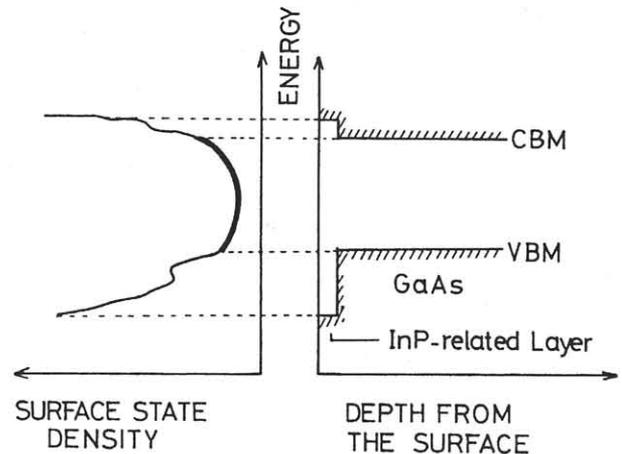


Fig.3 Schematic model of the band diagram for the TMI +  $PH_3$  treated surface. Only the states in the GaAs band gap (Bold Line) act as the effective surface states.

Fig.2, we estimated the thickness deposited by the CVD treatment to be about 1 nm, which is consistent with the amount of TMI supplied.

As we cannot determine the precise composition of this ultra-thin layer, we call it the InP-related layer.

### 3.3 Concept of Atomic Layer Passivation

Based on the above experiments, a new concept of surface passivation is proposed, as shown in Fig.3. This figure shows a schematic band diagram of this passivated GaAs surface with the ultra-thin InP-related layer. The band gap line-up model<sup>5)</sup> is considered in this model. Since the lattice constant of InP is larger than that of GaAs, the ultra-thin layer receives compressive stress. As a result, the conduction band minimum (CBM) of the layer becomes higher than the CBM of bulk InP as shown in Fig.3. This strain also causes a similar effect at

the valence band maximum (VBM), but in the opposite direction. Consequently, the band gap at the surface is much greater than the band gap observed for InP bulk.

The surface states of this structure should be determined by the surface states of the compound layer that are observed from the GaAs band gap window. Thus, the surface pinning of this system becomes weak when the surface state density becomes virtually very small and the surface (pinning) states of the compound layer resonate with the GaAs conduction band or valence band.

The above experimental results indicate that a thickness of a few atomic layers is enough for the passivation, which we call "Atomic Layer Passivation (ALP)".

The reason for the reduction of surface states in the GaAs band gap is not clear. However, it is plausible that the widening of potential regions between the GaAs VBM and the VBM at the surface or between the GaAs CBM and the CBM at the surface makes it easy for the states to move into these regions.

### 3.4 Case for Narrow Gap Layers

The band gap of an arsenic rich InAsP bulk is narrower than the band gap of GaAs. Curve C in Fig.1 corresponds to this As-rich InP-related layer structure. The surface treatment of the sample represented by curve C was similar to the treatment of the sample shown by curve A. For the curve-C sample, there was not enough time for As desorption from the GaAs surface. The PL intensity of this structure shows little enhancement, which verifies that ALP requires a wider gap layer.

### 3.5 Role of Layer Strain

Curve D in Fig.1 represents the surface treated without TMI. The surface layer was composed of Ga, As and P. In this case, no enhancement in the PL intensity was observed while the band gap of GaAsP was

Table I. Materials for ultra-thin layer and their strain and band gap characteristics. The combination of tensile with narrow band gap does not exist in the experiment using TMI and PH<sub>3</sub>.

		STRAIN	
		TENSILE	COMPRESSION
ENERGY GAP	NARROW	—	InPAs
	WIDE	GaAsP	InP In(Ga)(As)P

wider than the band gap of GaAs. This PL result indicates the importance of the strain effects described in the above model.

In the InP-related case (curve A) where the strain is compressive, we have seen that PL enhancement is remarkable. Therefore, we further regulated the amount of In to examine the strain effect. The curve-E sample was treated by about one-tenth of the TMI that was used to treat the sample represented by curve A. In this a little TMI case, PL intensity is enhanced but is degraded with time.

This In composition dependence on PL intensity suggests the necessity of compressive strain for ALP. The degradation seen in curve E is attributable to the release of compressive strain in the ultra-thin layer.

Our experimentation of the effect of an ultra-thin compound semiconductor layer from the view points of both the energy gap (band picture) and strain in the layer is summarized in Table I. At this point, the possibility that In atoms play a certain role in passivating the surfaces can not be excluded.

## 4. CONCLUSION

PL intensity is remarkably enhanced by utilizing an ultra-thin InP-related layer on GaAs surfaces. Results indicate that a thickness of a few atomic layers is enough for what we call "atomic layer passivation". This band picture is expected to serve as a new guide for surface passivation.

## REFERENCE

- 1) J. Fan, Y. Kurata and Y. Nannichi, J.J.A.P. **28** (1989) L2255.
- 2) H. Hirayama, Y. Matsumoto, H. Oigawa and Y. Nannichi, A.P.L. **54** (1989) 2565.
- 3) T. Sugino, T. Yamada and J. Shirafuji, Defect Control in Semicon. 1989 (Elsevier Science, North-Holland, 1990) p.849.
- 4) J. W. Matthews and A. E. Blakeslee, J. Cryst. Growth **27** (1974) 118.
- 5) H. Hasegawa and H. Ohno, J. Vacuum Sci. Technol. **1** (1986) 1130.