Extended Abstracts of the 19th Conference on Solid State Devices and Materials, Tokyo, 1987, pp. 471-474

Invited

Digital Epitaxy of III-V Compound Semiconductors

Akira Usui
Fundamental Research Laboratories, NEC Corporation
4-1-1 Miyazaki, Miyamae-ku, Kawasaki, Kanagawa 213, Japan

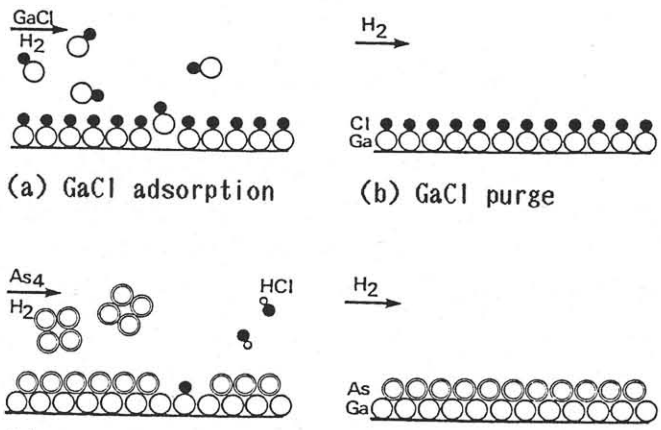
Atomic layer epitaxy (ALE) is presented as a novel growth technique with monolayer controllability. Experimental results show that ALE growth using GaCl or diethylgallium chloride, retains monolayer growth characteristics over a wide range of growth conditions. Such a growth is called "Digital Epitaxy". The digital nature of the growth is discussed using a Langmuir-type monolayer adsorption model. Atomic-plane doping using selenium as an impurity is demonstrated. Finally, delta-doped FET fabrication is presented as an device application. Transconductance as high as 215 mS/mm is obtained with a gate length of 0.5 μm.

1. Introduction

Atomic Layer Epitaxy (ALE), which was originally proposed by T. Suntola in 1977 [1], has been developed recently to a very attractive method to obtain monolayer-unit growth of III-V compound semiconductors [2-7]. Under specific growth conditions, the surface coverage of the source gas of group III element becomes unity with a self-limiting growth mechanism, and the growth proceeds with one atomic layer unit. Such a growth mode is called "Digital epitaxy". We used such group III element source gases as gallium chloride(GaCl) and diethylgallium chloride(DEGaCl), and hydride gases for group V elements. These chloride and metalorganic(MO) ALE systems have an excellent monolayer controllability with a self-limiting growth mechanism. This paper describes the achievement of digital epitaxy with discussions of the growth mechanism. Atomic-plane doping, and an application to δ-doped FET will be presented.

2. Growth Procedure in ALE

As an example, the ALE growth process for GaAs, using GaCl and As_4, is shown in Fig. 1. The first step (a) is an adsorption of the GaCl. After sufficient purging in the next step(b), an arsenic source gas is supplied into the substrate region(c). Unreacted arsenic compound gas and by-product gas are purged from the substrate region (d). Thus, a new GaAs layer is formed on the substrate.



(a) GaCl adsorption (b) GaCl purge

(c) Reaction (d) As_4 purge

Fig. 1 GaAs ALE growth process.

We used two kind of ALE growth apparatus; a multi-chamber-reactor using

chloride gases such as GaCl and InCl, and a MOCVD reactor using DEGaCl [8].

3. Achievement of Digital Epitaxy

In fig. 2, we summarize the ALE GaAs growth so far reported, from the viewpoint of the grown thickness controllability [5]. It is clearly shown here that the growth rates in the GaCl and DEGaCl ALE [8] lies approximately on this ideal growth rate line. GaCl partial pressure dependence of the growth rate has been investigated in the range of 10^{-4} to 10^{-3} atm, and the digital epitaxy was also confirmed. Besides GaAs, other III-V compounds such as InP, InAs, GaP and InGaP were successfully grown in monolayer units.

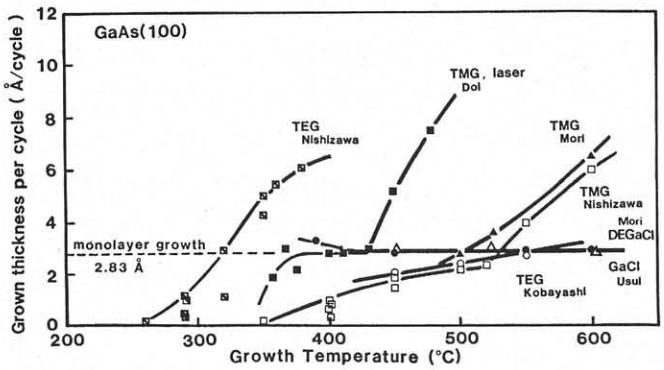


Fig.2 Growth temperature dependence of growth rate for ALE GaAs by various growth methods.

4. Discussion of Growth Mechanism

Here, we propose a Langmuir-type monolayer adsorption model for GaCl to explain the digital nature of the growth. It was reported by J. Korec that the GaCl adsorption energy on the (100)GaAs is 51.14 Kcal/mol and that the adsorption energy increases with increasing the GaCl surface coverage [9]. Using Korec's value and the isothermal equation for the Langmuir-type adsorption model($\theta = KP/(1+KP)$ K:adsorption equilibrium constant for GaCl, P: GaCl partial pressure), the GaCl surface coverage (θ) was calculated. Figure 3 shows the calculated results. At temperature less than about 500 °C, the coverage calculated is almost unity, when the GaCl partial pressure is greater than 10^{-4} atm. This result supports the digital nature of the chloride growth system. The strong GaCl adsorption excludes the adsorption of other species.

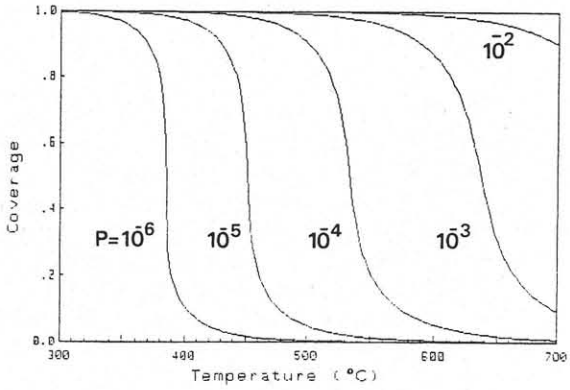


Fig. 3 GaCl coverage calculated by a Langmuir-type adsorption model.

Figure 4 shows the effect of free-HCl on the grown thickness of ALE GaAs. HCl gas was supplied simultaneously with GaCl.The effect of the free-HCl was almost negligible even for $P_{HCl}/(P_{HCl}+P_{GaCl})=0.55$. Such competitive adsorption may occur between GaCl and impurities and help to grow high-purity materials.

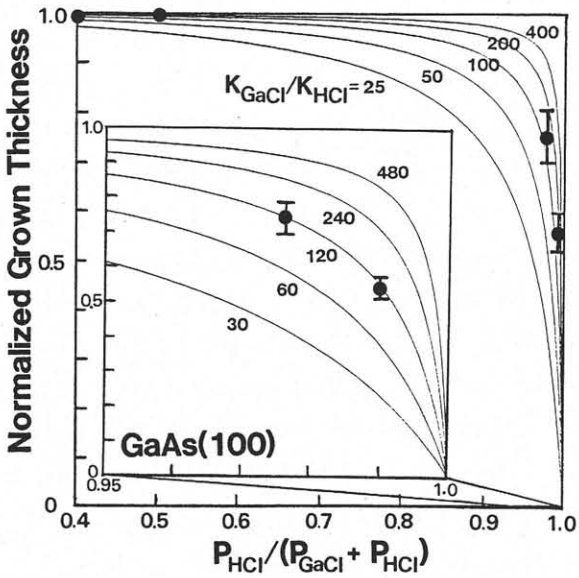


Fig. 4 Effect of free-HCl on the grown thickness of ALE GaAs.

In our typical growth condition of GaAs in GaCl-ALE, the impinging rate of GaCl onto the substrate was found to be in the 10^{18} to 10^{19} molecules/cm^2sec range. Since surface lattice sites for (100)GaAs are $6.4 \times 10^{14} cm^{-2}$, these surface sites is considered to be occupied with GaCl in a moment. The GaCl mean residence time (t) on the substrate can be estimated using the adsorption energy. This relationship is expressed as $t^{-1} = \upsilon \exp(-q/RT)$ [υ :the vibration frequency ($2.19 \times 10^{13} s^{-1}$), R:the gas constant]. The residence time is calculated to be greater than 3000 seconds at 450°C.

This concept can be basically applied to DEGaCl ALE. This is because DEGaCl decomposes easily to GaCl, and because the adsorption species are considered to be GaCl. Figure 5 shows the grown thickness uniformity over a 3-inch diameter substrate grown by the DEGaCl-ALE [8]. When the exposure time of DEGaCl to the substrate is 9 seconds, the uniformity is excellent in comparison with the results obtained in conventional MOCVD. This result supports the GaCl monolayer adsorption process in DEGaCl-ALE.

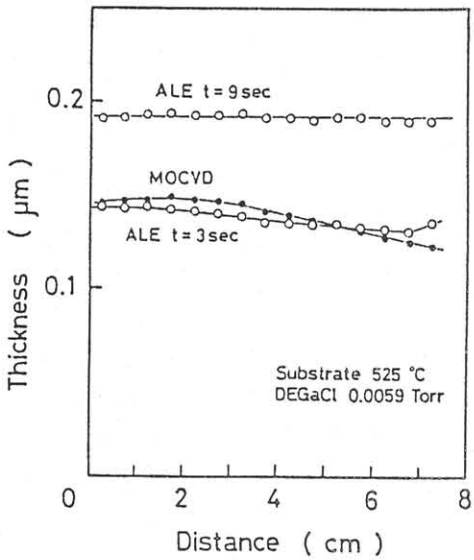


Fig. 5 Grown thickness uniformity in DEGaCl-ALE of GaAs

5. Atomic-plane Doping and Application to FET

Atomic-plane doping using selenium as an impurity was studied in ALE. H_2Se was used as the impurity source gas. We investigated the dependence of incorporated Se quantity on growth temperature and H_2Se partial pressure. At a 350 °C growth temperature, it was observed that the Ga surface was entirely covered with Se. A very steep carrier concentration profile with 8 nm of FWHM was obtained for a sample having one atomic impurity plane. Figure 6 shows the relationship between mobility and sheet carrier concentration obtained from atomic-plane-doped samples. As seen in this figure, the quality of ALE layers is comparable with that of MBE layers [10].

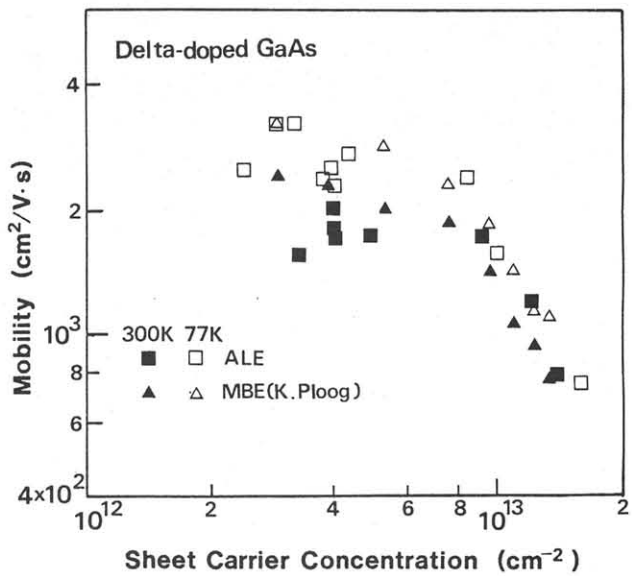


Fig. 6 Hall mobility versus sheet carrier concentration in the atomic-plane doping.

As an application, we fabricated δ-doped FETs [10,11] as shown in Fig. 7. Figure 8 shows the current-voltage characteristics of a delta-doped depletion mode FET with a gate length of 1 μm. A measured extrinsic transconductance was 190 mS/mm and this value was kept nearly constant above the pinch-off voltage. This shows that electrons are confined to the V-shaped potential well by the δ-doped structure. Furthermore,

transconductance as high as 215 mS/mm was obtained from a FET with a gate length of 0.5 μm.

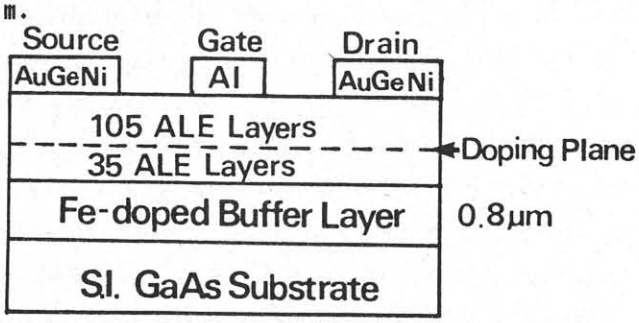


Fig. 7 Schematic structure of δ-doped FET.

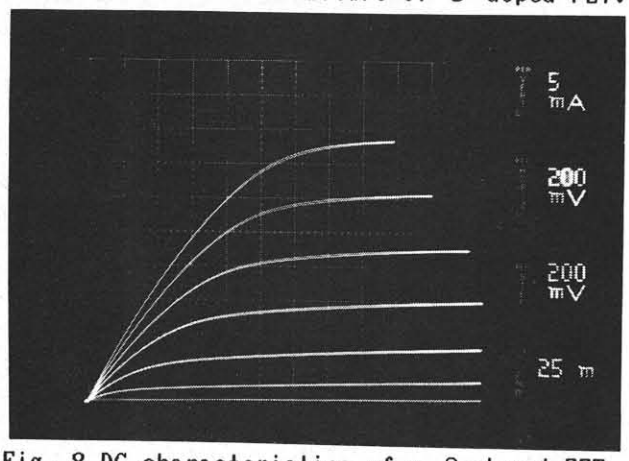


Fig. 8 DC characteristics of a δ-doped FET.

6. Summary

Digital epitaxy of III-V compounds has been presented as a novel method to control monolayer growth very accurately with self-limiting mechanism. ALE using chloride or metalorganic chloride source gas was found to be superior for achieving the digital epitaxial growth over a wide range of growth conditions. We discussed the growth mechanism using a Langmuir-type monolayer adsorption model. Excellent thickness uniformity was demonstrated here as an appreciable advantage of digital epitaxy. Atomic-plane doping using selinium and its application to a delta-doped FET with a high transconductance were presented. These results indicate that the present method has the potential to be developed as a new tool for preparing various sophisticated devices in the near future.

Acknowledgement

The authors would like to thank H. Sunakawa, K. Mori, H. Miyamoto for providing valuable data. The authors also thank M. Yoshida, H. Watanabe and M. Ogawa for helpful discussions and encouragement.

References

1. T. Suntola and M. J. Anton, US Patent No.4-058-430(1977).
2. J. Nishizawa, H. Abe and T. Kurabayashi, J. Electrochem. Soc. 132(1985)1197.
3. S. M. Bedair, M. A. Tischler, T. Katsuyama and N. A. El-Marsy, J. Appl. Phys. Lett. 47(1985)51.
4. N. Kobayasi, T. Makimoto and Y. Horikoshi, Jpn. J. Appl. Phys. 24(1985)L962.
5. A. Usui and H. Sunakawa, Jpn. J. Appl. Phys. 25(1986)L212.:
   H. Watanabe and A. Usui, Proceedings of the 13th International Symposium on GaAs and related Compounds 1986, Las Vegas,pl.:
   A. Usui and H. Sunakawa, ibid, p129.
6. K. Mori, A. Ogura, M. Yoshida and H. Terao Extended Abstracts of the 18th Conference on Solid State Devices and Materials, Tokyo, 1986, p743
7. A. Doi, Y. Aoyagi and S. Namba, Appl.Phys. lett. 49(13)785.
8. K. Mori, M. Yoshida, A. Usui and H. Terao, Abstracts of 1987 Spring Meeting of Jpn. Soc. Appl. Phys. p125.:
   Y. Yoshida, K. Mori, T. Sasaoka, H.Sunakawa, T. Matsumoto and A. Usui, Proceedings of Oyo DenshiBussei Bunkakai, No. 418 Meeting, 1987, p25(Japanese).
9. J. Korec, J. Cryst. Growth 60(1982)297.
10. K. Ploog, J. Cryst. Growth 81(1987)304.
11. E. F. Schubert, J. E. Cunningham and W. T. Tsang, Appl. Phys.Lett. 49(25)1729.
12. Y. Miyamoto, H. Sunakawa, A. Okamoto, A. Usui and K. Ohata, 1987 Abstract of 1987 Spring Meeting of Jpn. Soc. Appl. Phys.