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Pronounced Improvement of the Interface Property of Fluoride/GaAs Structures by Post-growth Annealing

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We show that post-growth annealing at high temperature can markedly improve the interface property of fluoride films grown by molecular beam epitaxy on GaAs(100). It has been found that the state densities of the CaF_2/GaAs interface derived from the Terman's method(1MHz C-V measurement) is reduced to about $5x10^{11}/cm^2eV$ after annealing typically at 850°C for 1 min., although the C-V curves still have a little frequency dispersion of the accumulation capacitance and some hysteresis loops. Ambient effect during annealing was investigated by measuring the structural and electrical properties of the films. Photoluminescence intensity of the CaF_2 coated GaAs was also measured before and after annealing.

1. Introduction

From viewpoints of fabrication of the very high speed and low power consumption integrated circuits, the GaAs MIS(metal-insulator-semiconductor) devices are expected to be a good candidate. Therefore, a number of GaAs MIS technologies[1] have been tried, however, none of them provides good interface properties enough to fabricate MISFET's(field effect transistors), mainly because of the existence of a large number of interface states within the bandgap.

Recently, heteroepitaxy of such crystalline insulator materials as alkaline earth fluorides(CaF_2, SrF_2 and BaF_2)[2-8] and lanthanum fluoride[9] was reported. In these systems, it is expected that the dangling bonds at the semiconductor surface are terminated by the atoms in the fluoride film, resulting in decrease of the interface state density. It is also expected that the contamination of the semiconductor surface is avoided by successive growth of a homoepitaxial GaAs layer and a heteroepitaxial fluoride film in an ultrahigh vacuum system. In this paper, we discuss the effect of post-growth annealing on interface property of fluoride films on GaAs(100) using the electrical and PL(photoluminescence) intensity measurements.

2. Experimental Procedure

Fluoride films such as CaF_2 and SrF_2 were grown in the MBE(molecular beam epitaxy) system which is composed of two growth chambers connected with a gate valve, one is used for the growth of GaAs and the other is for fluorides. Base pressure of both chambers is less than $3x10^{-10}$ Torr. In the experiments, heavily Si-doped n-type GaAs(100) wafers were chemically cleaned and etched in $3H_2SO_4/H_2O_2/H_2O$ solution. They were then mounted with In on a Mo block which served as an ohmic contact at the backside and loaded in the GaAs growth chamber. After thermal cleaning around 600°C in As atmosphere, n^+-buffer($2x10^{18}cm^{-3}$,1μm) and active ($6\text{-}9x10^{15}cm^{-3}$,1μm)layers were grown at 600°C with a typical growth rate of 1 μm/hour. The homoepitaxial samples were then transferred to the fluoride growth chamber maintaining ultrahigh vacuum and fluoride films about 100 nm thick were grown at temperature ranging from R.T. to 400°C with a growth rate of 0.1-0.2 nm/s.

After deposition of the fluoride films, each sample was cut in two parts and then one part was annealed at 800°C to 850°C for 1 to 3 min. in various gas ambient such as N_2, Ar, O_2 and H_2. Then, in order to measure the electrical properties of the films, MIS diodes were fabricated on both parts by depositing Al electrodes with diameters of 200 to 800 μm in vacuum. In order to further investigate the interface properties of the CaF_2/GaAs(100) structure, PL intensities of the annealed and unannealed samples were measured using Ar laser(514.5 nm) at 70K. In this experiment, the intensities were compared between the successive data for the two samples which were cooled simultaneously, so that the experimental error due to the different sample setup became minimum.

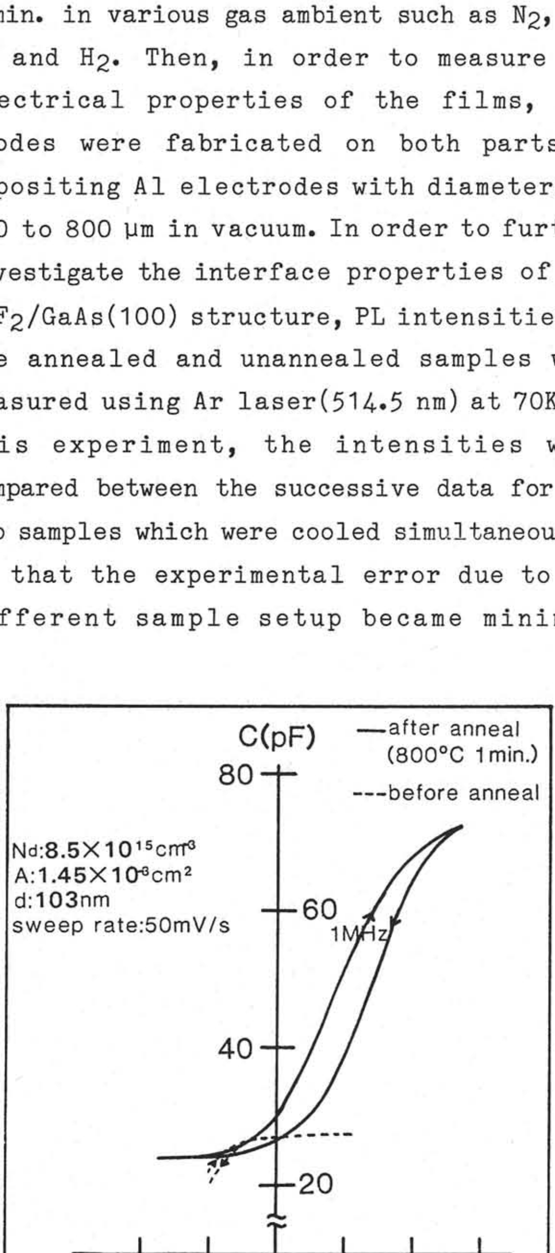

Fig.1 1MHz C-V characteristics of MIS diodes fabricated on the fluoride/GaAs(100) substrate.

Nomarski interference contrast microscopy and ellipsometry(546.1 nm) were also used to study the surface morphology and refractive index of the films.

3. Results and Discussion

Figure 1 shows 1MHz C-V characteristics of a MIS diode with CaF_2/GaAs interface, which was annealed at 800°C for 1 min. in N_2 atmosphere. The dashed curve is the characteristics of the as-grown sample and the solid curve is the post-growth annealed one which shows that the capacitance value varies from the accumulation to inversion states. The accumulation capacitance was experimentally measured by depositing the fluoride film on the n^+-GaAs layer under the same condition. Also, the breakdown voltage of the fluoride film was found to be improved from $5x10^5$V/cm of a typical value for as-grown films to $1x10^6$V/cm of that for the annealed ones. The increase of the breakdown voltage may be explained by improvement of the crystalline quality or densification of the film during annealing. In fact, it was observed that the refractive index of the films was increased by the annealing typically from 1.40 to 1.43. It was also found from the I-V measurement that the resistivity of the fluoride film was higher than $1x10^{13}$ Ωcm.

Interface state densities derived from the 1MHz C-V measurement(Fig.1) using the Terman's method is shown in Figure 2. The C-V curve from the inversion to accumulation states was used in the calculation. The result shows a U-shaped distribution in the bandgap and the minimum density around the midgap is about $5x10^{11}/cm^2eV$. Improvement of the breakdown voltage and the interface characteristics by post-growth annealing has also been reported in the CaF_2/Si(100)

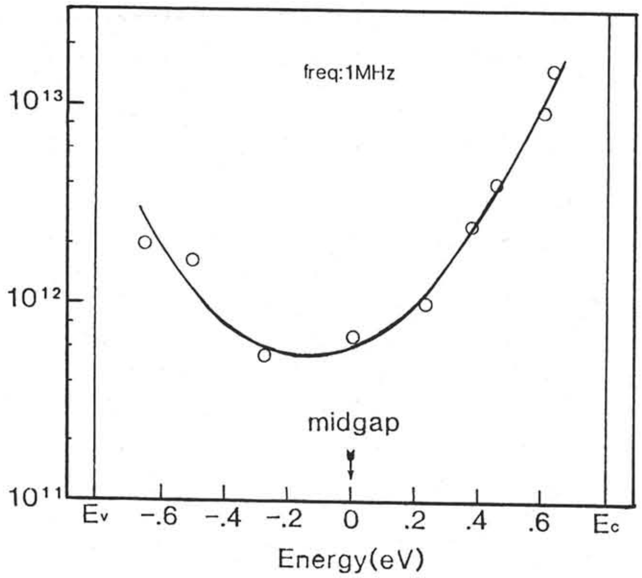

Fig.2 Interface state density distribution of the annealed sample derived from 1MHz C-V measurement using the Terman's method.

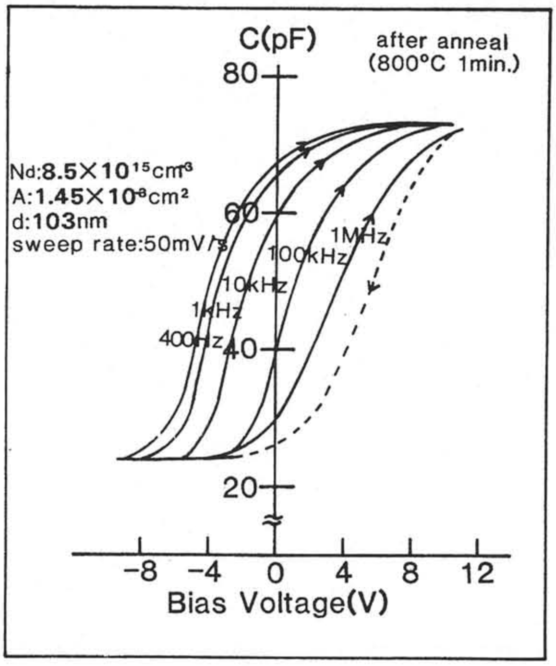

Fig.3 Frequency dependence of the C-V curve of the annealed sample.

system[10].

Figure 3 shows the dependence of the C-V curve on frequency ranging from 400Hz to 1MHz. It is noticed that the frequency dispersion is quite smaller in these frequency range compared with that of the oxide/GaAs MIS system[11]. In this particular sample, the hysteresis loop is the carrier injection type as shown in the figure. However, we often observed the ion drift type hysteresis. The origin of the hysteresis is not well understood at present.

In order to investigate the ambient effects during thermal treatment, the samples were annealed in various gases such as N_2, Ar, O_2 and H_2 atmosphere. Figure 4 shows the C-V curves of the samples annealed in various gas ambients. The annealing in N_2 or Ar gas ambient was effective to change the capacitance from the inversion to accumulation value. But the thermal treatment in O_2 or H_2 gas atmosphere made the diodes leaky rather than improved the C-V characteristics. It was also found that the surface morphology of the fluoride films

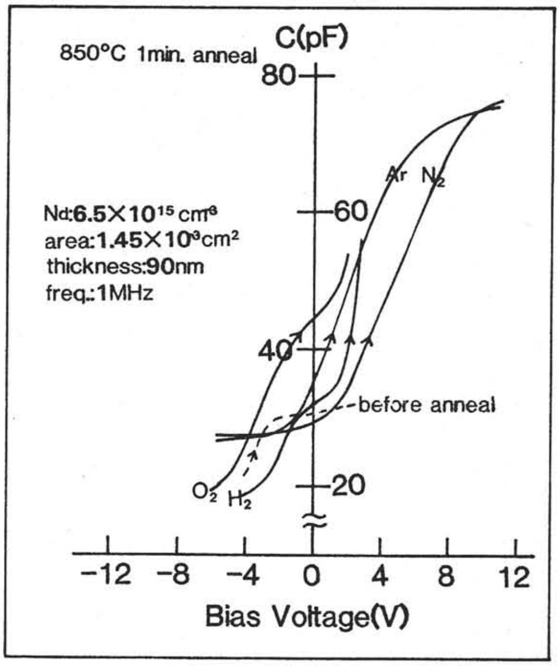

Fig.4 C-V curves of the samples which annealed in various gas ambients.

annealed in O_2 and H_2 ambient was rough and milky, which is probably due to the reaction between these gases and fluoride films. However, possibility of water vapor contamination in H_2 gas cannot be completely denied.

The PL intensity of the fluoride/GaAs samples gives another measure of the excellent interface properties. Figure 5 shows comparison of the PL intensities between the annealed and unannealed samples. It is seen that the intensity from the annealed sample is about 15 times stronger than the unannealed one. From this result, we speculate that the interface itself between the fluoride and GaAs was improved by the post-growth annealing, though it is necessary to continue more precise experiment in order to confirm the above speculation.

4. Conclusion

The post-growth annealing effects of MBE grown fluoride films on GaAs(100) was investigated. It was found from the electrical and optical measurement that the post-growth annealing is very useful in such improvement of the film and interface properties as increase of the breakdown voltage of the films, reduction of the interface state density, and so on. The improvement of the interface property may result in the rearrangement of the interfacial atoms due to dissociation of F atoms during the post-growth annealing.

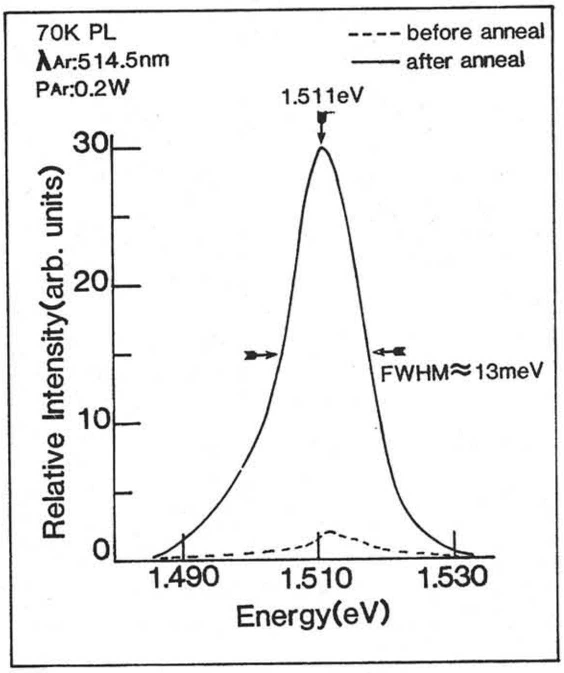

Fig.5 Comparison of PL intensities between the annealed and unannealed samples.

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References

[1]D. L. Lile,"Metal-Insulator-GaAs Structures in Gallium Arsenide Materials, Devices and Circuits, edited byM. J. Howes and D. V. Morgan,(Wiley & Sons, 1985), pp263-298

[2]R. F.C. Farrow, P. W. Sullivan, G. M. Williams, G. R. Jones and D. C. Cameron : J. Vac. Sci. Technol. 19(1981) 415

[3]H. Ishiwara and T. Asano : Appl. Phys. Lett. 40(1982) 66

[4]T. Asano, H. Ishiwara and N. Kaifu : Jpn. J. Appl. Phys. 22(1983) 1474

[5]T. Asano and H. Ishiwara : J. Appl. Phys. 55(1984) 3566

[6]S. Siskos, C.Fontaine and A. Munoz-Yague : J. Appl. Phys. 56(1984) 1642

[7]C. W. Tu, S. J. Wang, J.M.Phillips, J. M. Gibson, R. A. Stall and R. J. Wunder : J. Vac. Sci. Technol. B4(1986) 637

[8]H. Ishiwara, K. H. Kim, K. Tsutsui, T. Asano and S. Furukawa : Electrochemical Society 172nd Meeting, in Hawaii, oct. 1987, in Press

[9]S. Sinharoy, R. A. Hoffman, A. Rohatgi, R. F. C. Farrow and J. H. Rieger : J. Appl. Phys. 59(1986) 273

[10]Loren Pfeiffer, Julia M. Phillips, T. P. Smith,III, W. M. Augustyniak and K. W. West : Appl. Phys. Lett. 46(1985) 947

[11]T. Sawada and H. Hasegawa : Thin Solid Films 56(1979) 183