Dry Etching Characteristics of MOVPE Grown CdTe Epilayers in CH_4, H_2, Ar ECR Plasmas

K. Yasuda, M. Niraula*, N. Araki, M. Miyata, S. Kitagawa, M. Kojima, J. Ozawa,
S. Tsubota, T. Yamaguchi, and Y. Agata
Nagoya Institute of Technology, Graduate School of Engineering
Gokiso, Showa, Nagoya 466-8555, Japan
*Corresponding author: Tel: 81-52-735-5605, Email: m.niraula@nitech.ac.jp

Abstract:

Dry etching characteristics of single crystal (100) CdTe epitaxial layers grown on GaAs substrates were studied using CH_4, H_2, and Ar as process gases in an electron cyclotron resonance (ECR) plasma. A smooth and anisotropic etching was obtained with CH_4, H_2, and Ar. No hydrocarbon polymer was found on the etched surface, which was confirmed by X-ray photoelectron spectroscopy measurement. Etching of the CdTe surface was also possible with H_2 and Ar, however, no etching was observed in the absence of H_2. Dependence of the etch rate on plasma gas composition and flow rates were studied. Mechanisms of etching with and without CH_4 supply were also studied. Etched CdTe layers also showed no deterioration of the electrical properties, which was confirmed by photoluminescence measurement at 4.2 K and the Hall measurement at 300K.

Keywords: CdTe, ECR plasma, etching characteristics,

I. INTRODUCTION

We have been developing radiation detectors with energy discrimination capability using thick single crystal CdTe layers grown on Si substrates by metalorganic vapor phase epitaxy (MOVPE). [1-3] The detector is a heterojunction diode type with p-like CdTe/n-CdTe/n+-Si structure. We have also fabricated 8x8, 2-dimensional detector arrays by integrating the above diode detectors.[4] The detector array was fabricated by isolating each pixel by deep trenches, which were formed on the CdTe surface using a dicing saw. Trenches were formed in X and Y directions on the CdTe surface, and the depth was about 250 μm from CdTe surface to half of the Si thickness. Successful performance has obtained.[5] The trench width of 20 μm is achievable with the dicing saw, however, alternative formation techniques of narrow and deep trenches are desired for detector arrays with high density of integration. As a candidate of such techniques we have reported laser ablation using a shadow mask.[6] However, there was difficulty in fabricating metal shadow mask with micrometer size dimension. The other candidate is electron cyclotron resonance (ECR) plasma dry etching. Since low ion-induced damage in ECR plasma etching has been reported, fabrication of detector arrays with low dark currents at bias condition around several 100 V may be expected. [7-9]

In this paper, we have studied dry etching properties of single crystal (100) CdTe layers using ECR plasmas with CH_4, H_2 and Ar gases. Here we report on the dependence of the etch rate on gas composition, compositional properties of the etched surface as well as the effect of the etching on electrical properties of CdTe layers.

II. EXPERIMENTAL

Figure 1 shows schematic diagram of the etching system used in this study. The chamber is equipped with an ECR plasma source (2.45 GHz) and permanent type magnets. The plasma was generated at a microwave power of 600W, and at a chamber pressure of 0.267 Pa. The microwave power density on the slotted antenna was 1.9 W/cm^2. Process gases used were a mixture of CH_4, H_2, and Ar. The H_2 and Ar were introduced into the plasma zone (upstream), while CH_4 was fed downstream (above the substrate holder). The flow rate of all process gases were controlled with individual mass-flow controllers. The samples were placed on a water cooled substrate holder and kept at room temperature. The self-bias voltage was cancelled by applying a DC bias to the substrate holder.

Etching samples used were single crystal (100) CdTe layers, which were grown on (100) GaAs substrates by metalorganic vapor phase epitaxy (MOVPE). Mask patterns were formed on the sample with positive-type photoresist using standard photolithography. The etch rate was measured from cross-sectional images of the patterned samples which were obtained by scanning electron microscopy (SEM). SEM was also used to characterize the surface morphology of the

etched samples. X-ray photoelectron spectroscopy (XPS) measurement was carried out to characterize the etched surface. Influences of etching on the electronic properties of CdTe layers were also evaluated by photoluminescence (PL) measurement at 4.2 K and Hall measurement at 300K.

III. RESULTS AND DISCUSSION

1. Etching Characteristics

Figure 2 shows the dependence of etch rate as a function of CH_4 flow rate, where flow rate of H_2 is a parameter, and flow rate of Ar was kept constant at 1.5 ccm. At the H_2 flow rate of 1.9 ccm, the etch rate remained almost constant at 120 nm/min for low CH_4 flow rates from 0.5 to 2.0 ccm, however, it decreased to zero when the flow rate was increased to 5.0 ccm. When the H_2 flow rate was increased to 4.0 ccm, a slight increase in the etch rate was observed up to CH_4 flow rate of 2.0 ccm. However, the etch rate also decreased in the similar manner as that observed for H_2 flow rate of 1.9 ccm. Moreover, etching was clearly observed with H_2 and Ar supply (i.e. when CH_4 flow rate was zero).

Here, we discuss the observed etching characteristics by separating them into two parts. First, the etch-stop at higher CH_4 flow rates suggests possibility of hydrocarbon polymer formation on the CdTe surface as reported previously.[9,11] Second, the etching of the CdTe crystals observed even in the absence of the CH_4 suggests sputtering effects by the Ar^+-ions.

In order to investigate the possibility of hydrocarbon polymer formation of the sample surface, we examined the plasma etched CdTe surface using an XPS. The sample was etched using CH_4, H_2 and Ar flow rates at 5.0, 1.9 and 1.5 ccm, respectively. Fig. 3 shows the wide scan XPS spectrum and C1s spectrum in details. The result indicates that strong Te3d and Cd3d peaks with similar intensities, and small carbon and oxygen related peaks are detected. The high resolution scan of C1s peak mostly exhibits one single peak, and there is no chemical shift due to C-H hydrocarbons. Based on the binding energy of the observed peak, this carbon is considered as adsorbed on the CdTe surface during the transport of sample from etching chamber to analyzer. Hence, it is very unlikely that the hydrocarbon polymer is formed on the CdTe surface that stopped the etching in our system. The etch-stop observed at high CH_4 flow is due to other reason which is not clear at this moment. One possibility could be some gas phase reactions that prevent the formation of methyl radicals, but this will need verification.

To investigate the sputtering effect of the Ar^+-ion, we studied CdTe etching using a constant Ar flow, where the H_2 flow was varied from 0 to 4.0 ccm, without using CH_4. The result is shown in Fig. 4, which clearly indicates that the etching rate increases with the H_2 flow rate. But when the H_2 flow rate was decreased to zero and only Ar was supplied at 1.5 ccm, the etching rate of CdTe also decreased to zero. This result indicates that the etching of CdTe is not due to the

sputtering effect of the Ar-ions, but primarily due to the chemical reaction of H_2 with CdTe.

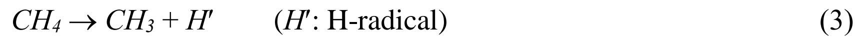
Based on the above results we would like to discuss the possible mechanism of CdTe etching. The etching of CdTe can be described by the following reaction model[12,13].

<u>Without CH_4 in the plasma (H_2 and Ar plasma only):</u>

$$CdTe + 2H \rightarrow Cd + H_2Te \quad (1)$$

$$Cd \rightarrow Cd_{vapor} \text{ (Thermal desorption)} \quad (2)$$

<u>$CH_4/H_2/Ar$ plasma:</u>



$$CH_4 \rightarrow CH_3 + H' \qquad (H'\text{: H-radical}) \quad (3)$$

$$H_2 \rightarrow H' + H' \quad (4)$$

$$CdTe + 2CH_3 + 2H' \rightarrow Cd(CH_3)_2 + H_2Te \quad (5)$$

In the former case when the CH_4 is not present in the plasma, atomic hydrogen reacts with CdTe forming elemental Cd and volatile H_2Te. The Cd is then removed from the surface by thermal desorption, where the energy required is provided from the Ar^+-ions[13]. However, it should be noted that Ar+-ion energy alone is not sufficient to etch the CdTe and hydrogen is the primary etchant as shown in Fig. 4. The etching mechanism is different when the CH_4, H_2 and Ar are present. In the latter case, H and CH_3 radicals are formed by the plasma. They react with CdTe forming volatile dimethylcadmium and H_2Te, which are easily removed from the crystal surface.[7,10-12] The role of Ar is to ease the ignition of the plasma discharge.[7,12]

The surface morphology of the etched sample in the presence and absence of CH_4 in the plasma is shown in Fig. 5, at constant H_2 and Ar flow rates. The flow rates of CH_4, H_2 and Ar were 3.0, 1.9 and 1.5 ccm, respectively. The result shows the surface morphology becomes somewhat better when CH_4 is present. This could be due to the difference in the etching mechanism as discussed above.

2. Etching effect on electrical properties of crystal

The effect of plasma etching on the electrical properties of the CdTe crystals was also investigated. As an etching sample, we used an iodine-doped n-type CdTe layer grown on the GaAs substrate. Table I shows the van der Pauw Hall measurement data of the sample before and after the plasma etching. The samples were etched in H_2 and Ar supply for 10 min, which approximately removes 1.0 μm thick layer from the surface. A slight increase in electron density and mobility was observed but the conductivity type of the crystal remained unchanged as n-type, according to the Hall data. Fig. 6 shows PL spectra of CdTe sample before and after etching. The PL spectrum of the sample before etching exhibits a sharp (D^o, X) emission peak, less pronounced

(A^o, X) peak along with DAP emission at 1.4 to 1.5 eV range. After etching the (D^o, X) emission decreases, but the intensity of the (A^o, X) and the DAP emission remains unchanged. Moreover, their peak positions also remain similar. These results indicate that the effect of etching on the electrical properties of the CdTe layer is minimal. However, it is not clear the reason behind the reduction of (D^o, X) peak intensity at this moment. It may be some surface phenomenon, as the etching with H_2 and Ar had resulted in a somewhat rough surface, but this needs further verification.

IV. CONCLUSION

Dry etching characteristics of single crystal (100) CdTe epitaxial layers grown on GaAs substrates was studied using CH_4, H_2, and Ar in an electron cyclotron resonance (ECR) plasma. A smooth and anisotropic etching was obtained with CH_4, H_2, and Ar, where etching rate decreased with increase of CH_4 supply. No hydrocarbon polymer was formed on the etched CdTe surface as confirmed by XPS measurement. The etching of CdTe was also possible with H_2 and Ar (without CH_4), where the etching rate was dependent on the H_2 flow rate. However, no etching was observed when only Ar was supplied (without H_2 supply). This suggested that sputter-etching by Ar^+-ion was absent in the above etching process. Surface smoothness improved when CH_4 as added in the process gas. Mechanisms of etching with and without CH_4 supply were also studied. No deterioration of electrical properties after etching was confirmed by the PL and the Hall measurements.

REFERENCES

1. K. Yasuda, M. Niraula, K. Noda, M. Yokota, H. Ohashi, K. Nakamura, M. Omura, I. Shingu, S. Minoura, R. Tanaka, and Y. Agata, *IEEE Electron Device Lett.* 27, 890 (2006).
2. M. Niraula, K. Yasuda, K. Noda, K. Nakamura, I. Shingu, M. Yokota, M. Omura, S. Minoura, H. Ohashi, R. Tanaka, and Y. Agata, *IEEE Trans. Nuclear Science* 54, 817 (2007).
3. M. Niraula, K. Yasuda, A. Watanabe, Y. Kai, H. Ichihashi, W. Yamada, H. Oka, T. Yoneyama, H. Nakashima, T. Nakanishi, K. Matsumoto, D. Katoh, and Y. Agata, *IEEE Trans. Nuclear Science* 56, 836 (2009).
4. M. Niraula, K. Yasuda, S. Namba, T. Kondo, S. Muramatsu, H. Yamashita, Y. Wajima, and Y. Agata, *IEEE Trans. Electron Devices* 59, 3450 (2009).
5. M. Niraula, K. Yasuda, N. Fujimura, T. Tachi, H. Inuzuka, S. Namba, T. Kondo, S. Muramatsu, and Y. Agata, *IEEE Trans. Nucl. Sci.* 59, 3201 (2014).
6. K. Yasuda, M. Niraula, K. Nakamura, M. Yokota, I. Shingu, K. Noda, Y.Agata, K.Abe, and O.Eryu, *J. Electron. Mater.* 36, 837 (2007).
7. S. J. Pearton and F. Ren, *J. Vac. Sci. Technol* B 11, 15 (1993).
8. R. C. Keller, M. Seelman Eggbert, and H. J. Ritchter, *J. Electron. Mater.* 24, 1155 (1995).
9. J. D. Benson, A. J. Stoltz, A. W. Kalaczyec, M. Martinka, L. A. Almeida, P. R. Boyd, and J. H. Dinan, *J. Electron. Mater.* 31, 822 (2002).
10. C. R. Eddy, Jr., D. Leonhardt, V. A. Shamamian, J. R. Meyer, C. A. Hoffman, and J. E. Butler, *J. Electron. Mater.* 28, 347 (1999).
11. R. C. Keller, M. Seelman Eggbert, and H. J. Ritchter, *J. Electron. Mater.* 25, 1270 (1996).
12. R. C. Keller, H. Zimmermann, M. Seelman Eggbert, and H. J. Ritchter, *J. Electron. Mater.* 26, 542 (1997).
13. A. J. Stoltz, M. Jaime-Vasquez, J. D. Benson, J. B. Varesi, and M. Martinka, *J. Electron. Mater.* 35, 1461 (2006).

Table Caption:

Table I. Hall measurement data of CdTe crystal before and after plasma etching

Figure Captions:

1. Schematic drawing of the plasma etching chamber
2. Etch rate of CdTe layers as a function of CH_4 flow rate
3. Wide scan XPS spectrum of plasma etched CdTe surface (a), and high resolution C1s spectrum (b). The etch was performed at 600W, 0.267 Pa pressure using a mixture CH_4, H_2 and Ar gases with flow-rates of 5.0, 1.9 and 1.5 ccm, respectively.
4. Etch rate of CdTe layers as a function of H_2 flow rate
5. Surface morphologies of the etched samples in the absence (a) and presence of CH_4 gas in the plasma (b). The flow rates of H_2 and Ar were constant at 1.9 and 1.5 ccm, respectively; the flow-rate of CH_4 was 0 in (a), whereas it was 3.0 ccm in (b).
6. The 4.2K PL spectra of the iodine-doped CdTe layers. (a)As-grown sample (before plasma etching), and (b) after etching in the H_2 and Ar plasma.

Table I.

Sample condition	Electron density (cm^{-3})	Mobility (cm^2/V.s)
Before etching	5.46×10^{14}	64
After etching	7.17×10^{14}	118

K. Yasuda et al.

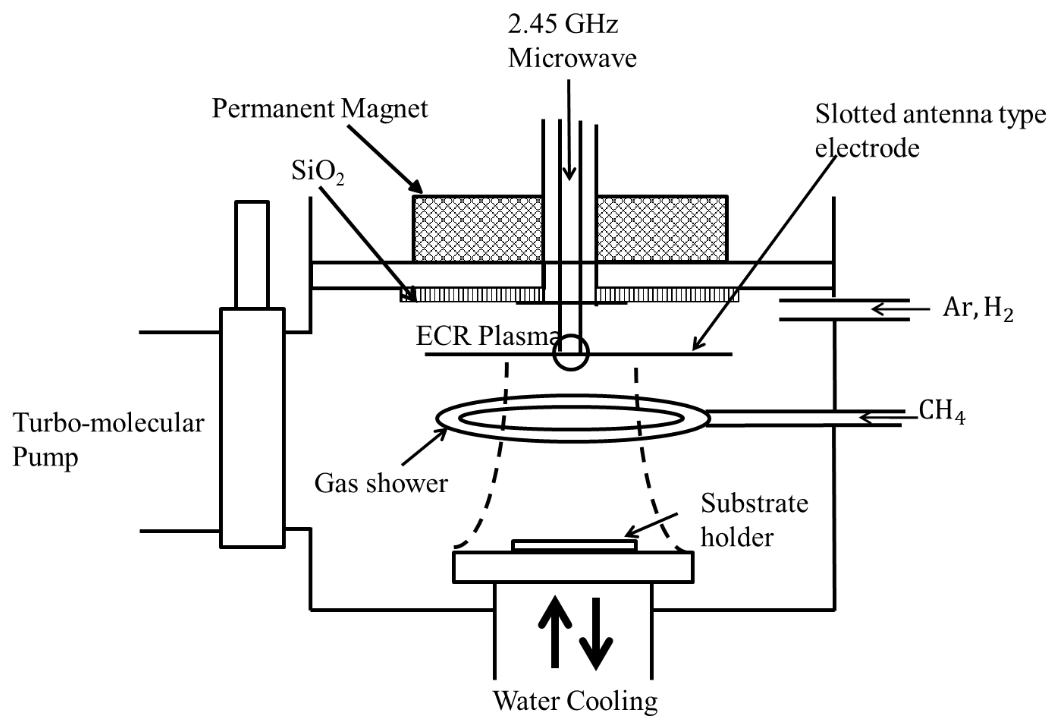


Fig. 1

K. Yasuda et al.

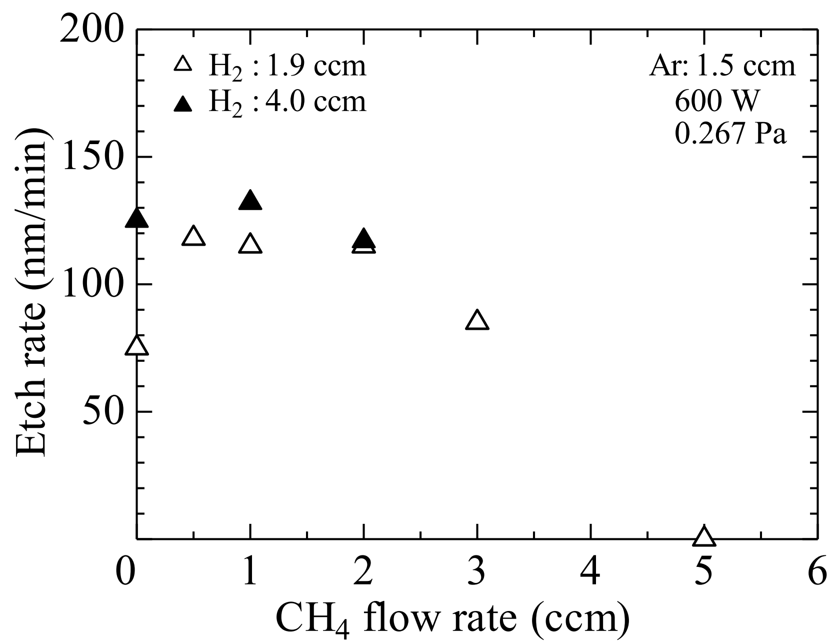


Fig. 2

K. Yasuda et al.

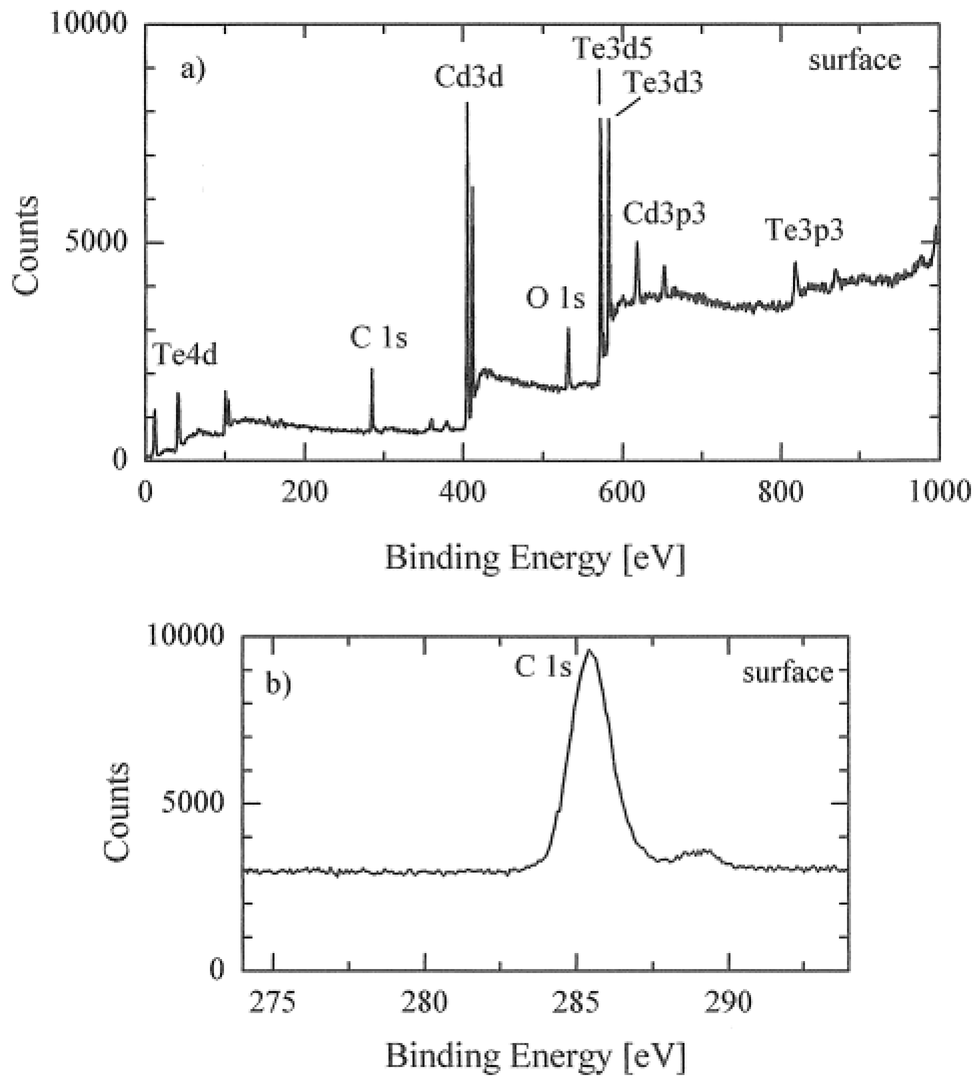


Fig. 3

K. Yasuda et al.

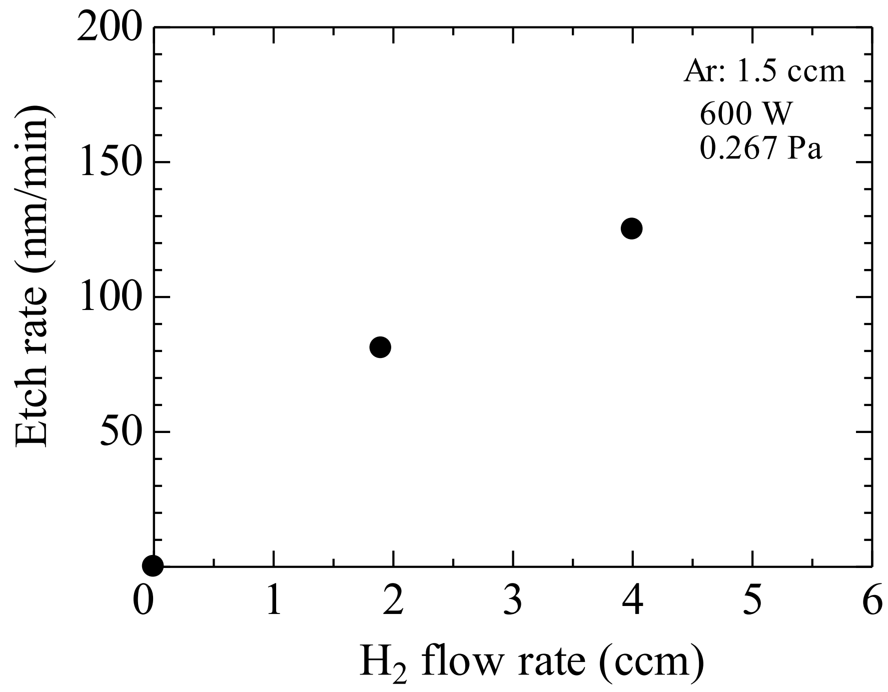
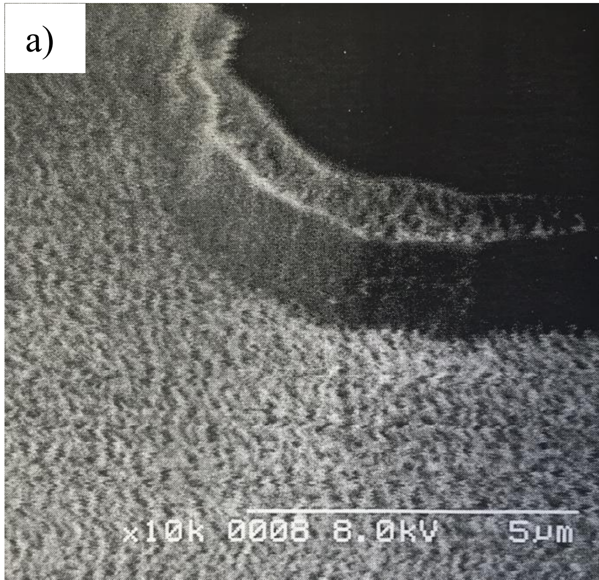


Fig. 4

K. Yasuda et al.



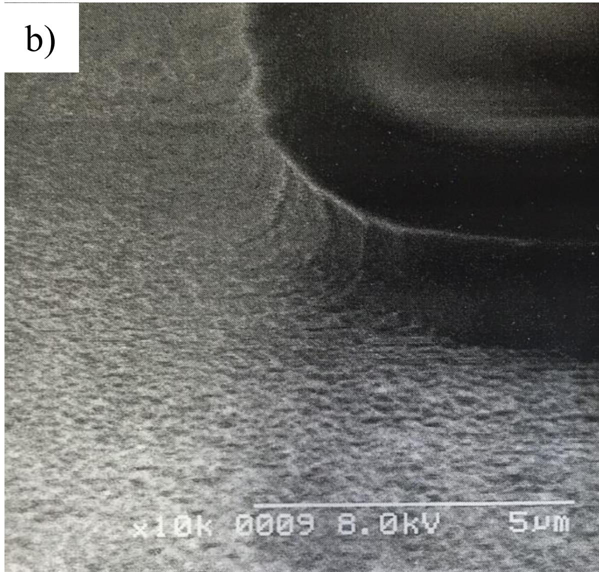


Fig. 5

K. Yasuda et al.

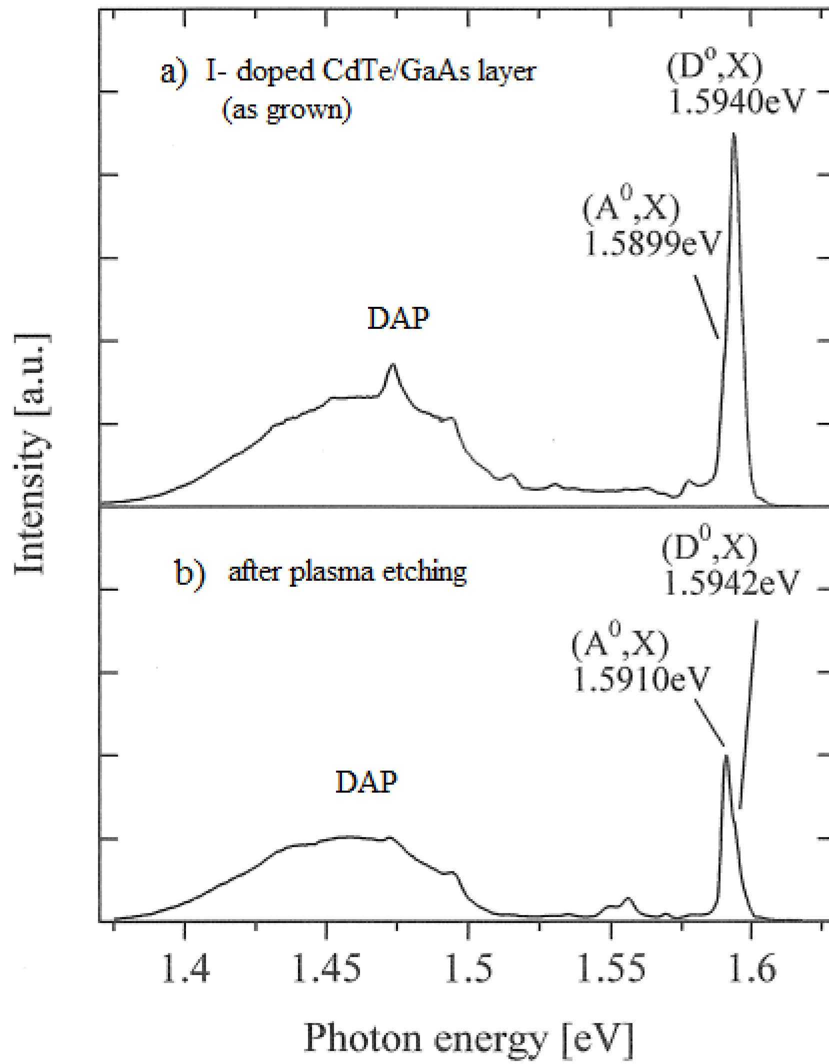


Fig. 6

K. Yasuda et al.