New Surface Treatment Method for Improving the Interface Characteristics of CdTe/Hg$_{1-x}$Cd$_x$Te Heterostructure

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This paper presents a new simple method of HgCdTe surface treatment which consists of chemical oxidation of HgCdTe with nitric acid and removal of the oxide with ammonium hydroxide. The electrical properties of the electron-beam deposition CdTe passivation of Hg$_{0.7}$Cd$_{0.3}$Te are investigated with regard to the effects of HgCdTe surface etching, exposure to nitric acid, and the new surface treatment method. As the HgCdTe surface is progressively etched with bromine in methanol (Br-MeOH), the surface becomes rougher and a higher density of fixed charge is induced at the interface between CdTe and HgCdTe. Exposure to HNO$_3$ results in a very high density of fixed charge and performance degradation in metal insulator semiconductor (MIS) capacitors, which is due to the chemical oxide grown by HNO$_3$. The oxide growth rate is enhanced as the concentration of HNO$_3$ increases or as more H$_2$O is added. This oxide can be removed with NH$_4$OH. After the new surface treatment, MIS capacitors of Hg$_{0.7}$Cd$_{0.3}$Te show substantial improvement in electrical properties, such as low density of fixed charge and reduced hysteresis width, regardless of previous surface etching.

INTRODUCTION

Among various materials, CdTe has recently been emerged as a very promising one for passivation of HgCdTe photodetectors.[1-4] Its low conductivity, near lattice match, and chemical compatibility with HgCdTe are expected to yield low defect densities and hence a low surface state density at the interface. The requirements of a good passivation for HgCdTe photodiodes and the features of the CdTe/HgCdTe heterostructure are well addressed by Y. Nemirovsky.[5]

However, HgCdTe surface passivation is very complex and difficult because of the narrow band gap, compound nature of the semiconductor, and also due to the tendency of electrically active defects to form in the interface region during passivation. The HgCdTe surface may also be nonstoichiometric, contaminated,

and damaged in crystallinity. The chemical, structural, and electronic defects induce a high density of fixed, fast, and slow interface traps which are usually responsible for the excessive dark currents and high noise level of the photodiode.[6,7]

Thus, appropriate surface preparation is required and is very important for good CdTe passivation of HgCdTe. Usual surface preparation methods for bulk HgCdTe wafers are chemo-mechanical polishing or mechanical polishing followed by chemical etching with bromine etchants in various solvents (methanol, ethylene glycol, dimethyl formamide). Organic chemicals and dilute acids can be used to clean the HgCdTe surface. However, above surface preparation methods are not enough to obtain clean and stoichiometric HgCdTe surfaces because the bromine etch enriches the HgCdTe surface in Te and Hg and depletes it in Cd. This Te-enriched surface layer is easily oxidized when exposed to air or acids, and this native oxide is one of the main causes degrading the passivation properties. In addition, the HgCdTe surface may be

contaminated in particular, by particles or residues of photoresist during device fabrication processes. In this case, it is very difficult to completely remove the contamination only with a bromine etch, organic chemicals and dilute acids.

Therefore, an additional surface treatment step is required. M. Seelmann-Eggebert et al. proposed a photochemical oxidation step after the bromine etch.[8] However, an application to HgCdTe passivation was not included in their study, and their method needs an additional vacuum process and so complicates the HgCdTe surface processing. In this paper, a new surface preparation procedure is presented and characterized.

EXPERIMENTS

Solid state recrystallized p-type bulk Hg$_{0.7}$Cd$_{0.3}$Te wafers with hole concentration of about 1×10^{16} cm^{-3} were used for all the experiments. The wafers were polished before experiments. A new procedure for the HgCdTe surface preparation was developed, which is composed of chemical oxidation of HgCdTe with nitric acid (HNO$_3$) and removal of the oxide with ammonium
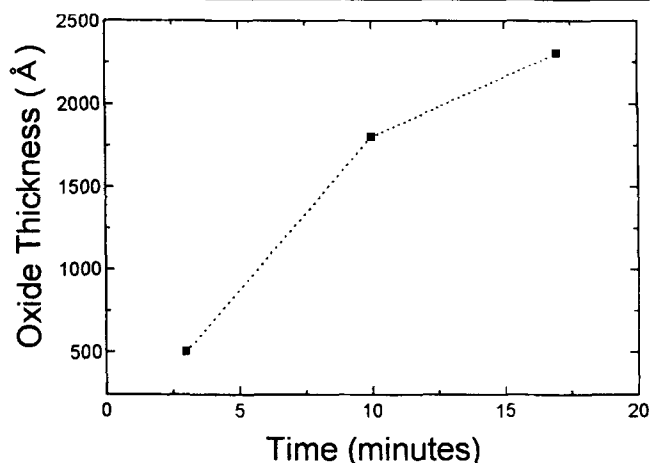

Fig. 1. Oxide thickness vs process time. The chemical oxide was grown on a Hg$_{0.7}$Cd$_{0.3}$Te wafer with HNO$_3$:H$_2$O$_2$ = 3 : 1 solution at room temperature.

hydroxide (NH$_4$OH). The chemical oxide and its effects on the electrical properties of CdTe passivation of HgCdTe were examined using scanning electron microscopy (SEM) and metal insulator semiconductor (MIS) capacitors. Using atomic force microscopy (AFM), we investigated the HgCdTe surface morphology and also the changes of the morphology after bromine-in-methanol (Br-MeOH) etch and the new surface preparation. In order to examine the effects of the new surface treatment method on the electrical properties of CdTe passivation, MIS capacitors with ZnS/CdTe double passivation layer were fabricated and characterized. The double layer consisted of thin CdTe film (500~1000Å) on HgCdTe and thick ZnS (~3000Å) on the CdTe film. CdTe was electron beam evaporated at the rate of 30Å/min below 2×10^{-6} Torr with the HgCdTe wafer at room temperature.

RESULTS AND DISCUSSIONS

Chemical Oxidation and Removal of the Oxide

It is known that dilute acids of HNO$_3$, HCl H$_2$SO$_4$, and lactic acid make the HgCdTe surface chemically passivated by the coverage of up to a monolayer of a native oxide.[8] We varied the degree of chemical oxidation by changing the concentrations of acids and the process time. From experiments, we found that HNO$_3$ most readily oxidizes the HgCdTe surface and that even thick oxide films can be easily grown. The oxidation rate strongly depends on the concentration of HNO$_3$ and is enhanced by the addition of H$_2$O$_2$.

Figure 1 shows the change of the oxide thickness grown on a bulk Hg$_{0.7}$Cd$_{0.3}$Te with HNO$_3$:H$_2$O$_2$ = 3:1 solution at room temperature. The oxide thickness was measured with a stylus profiler. About 2300Å thick oxide was grown in only 17 min. Figure 2 shows the SEM images of the chemical oxide which was grown in HNO$_3$:H$_2$O$_2$ = 1:1 solution for 10 min. The oxide is about 2400Å thick and has granular structure.

As mentioned in the introduction, the HgCdTe surface may be contaminated by particles or pho-
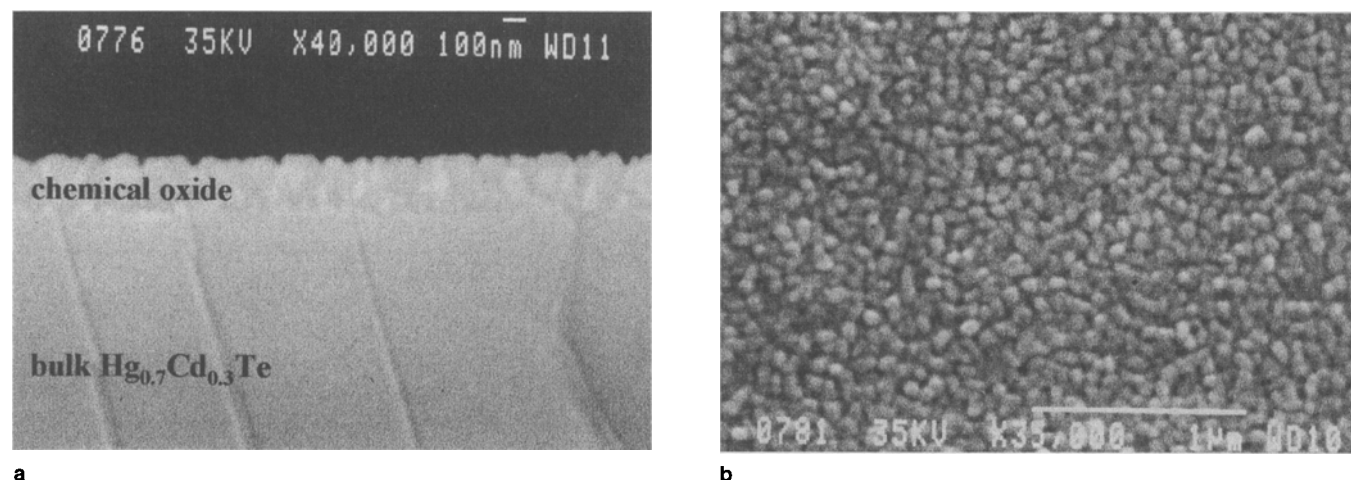

a   b

Fig. 2. SEM images of an oxide layer grown on a bulk Hg$_{0.7}$Cd$_{0.3}$Te in HNO$_3$:H$_2$O$_2$ = 1:1 solution for 10 min at room temperature. (a) cross-sectional view of a cleaved sample, and (b) plane view of the oxide.
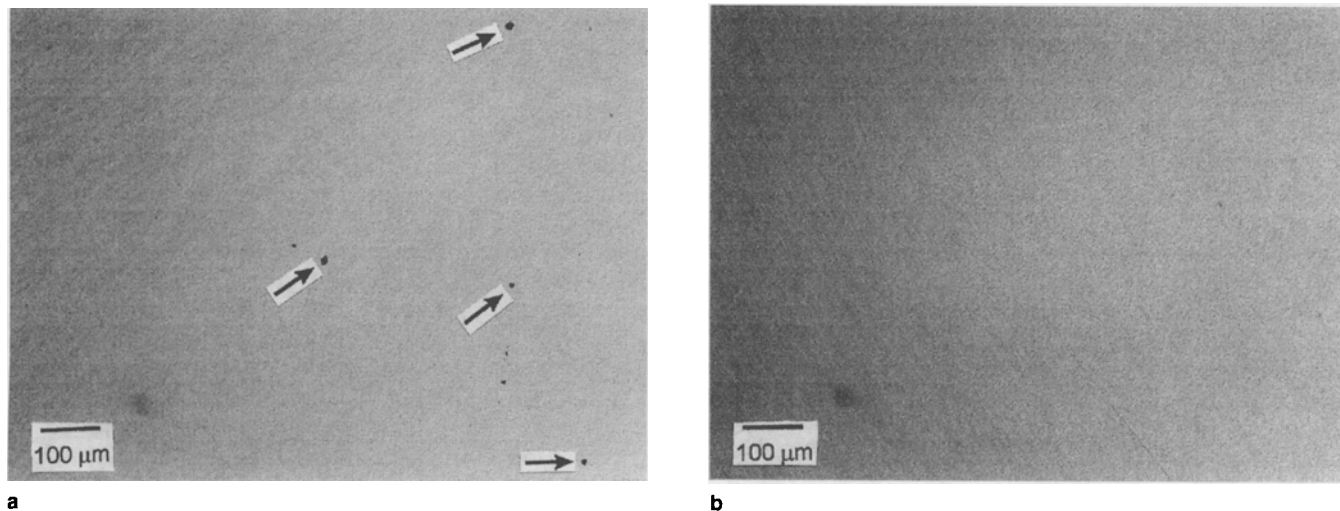
Fig. 3. Photomicrographs of HgCdTe surfaces (a) cleaned with organic chemicals and HCl, and (b) after treated with the procedure of chemical oxidation and removal of the oxide. The arrows in (a) point to the particles.

toresist residues during device fabrication processes. These are not removed well only with dilute acids and organic chemicals. However, strong HNO_3 can make the HgCdTe surface cleaner than the organic chemicals or dilute acids, as shown in Fig. 3. Figure 3a is the photomicrograph of a HgCdTe surface which was cleaned two times with organic chemicals and HCl, but there still remain some particles. These particles will drastically degrade the passivation quality if not completely removed. Figure 3b is the photomicrograph of the same HgCdTe surface after it was immersed in strong HNO_3 for 10 min and then the chemical oxide was removed. It is seen that all the particles are removed. Thus, without additional complicated processes, we can obtain cleaner HgCdTe surfaces with the simple procedure of chemical oxidation and removal of the oxide.

To examine the effect of the chemical oxide on the electrical properties of CdTe passivation of HgCdTe, MIS capacitors were fabricated and characterized. The MIS capacitors were fabricated on bulk $Hg_{0.7}Cd_{0.3}Te$ after immersing it in 7 M HNO_3 for 30 s at room temperature. As the passivation layer, 1000Å thick CdTe was electron-beam evaporated on the HgCdTe and 3000Å thick ZnS was evaporated on the CdTe. Figure 4 shows a hysteresis capacitance-voltage (C-V) curve of the MIS capacitor. It was measured at 77K with 1 MHz frequency. It does not look normal and exhibits high density of fixed charge, 4×10^{11} cm^{-2}. Thus, the complete removal of the chemical oxide is very important to obtain a near flatband condition in the interface region.

The removal of chemical oxide is achieved simply with NH_4OH not with acids. However, the oxide etch rate is too slow. Thus, a mixed solution of NH_4OH, H_2O, and H_2O_2 was used to increase the etch rate. Care must be taken at this step since this solution also generates an anomalous layer on the HgCdTe surface. So, we used a two-step oxide removal process. At first, most oxide is etched with the mixed solution of NH_4OH, H_2O, and H_2O_2, then the remaining oxide is
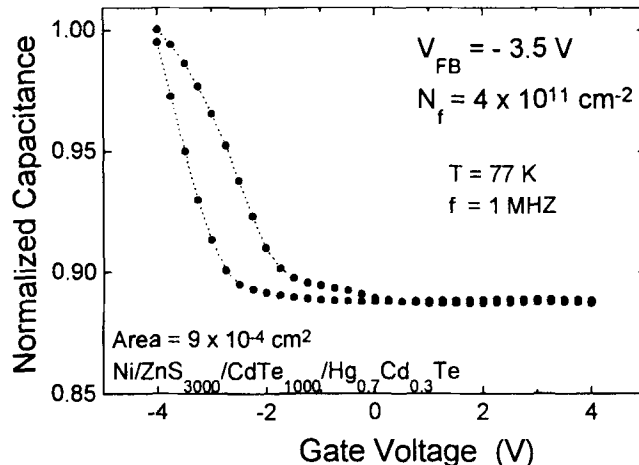

Fig. 4. A C-V curve of a ZnS/CdTe double layer MIS capacitor fabricated on a $Hg_{0.7}Cd_{0.3}Te$ wafer treated with 7 M HNO_3 for 30 s.

completely removed with NH_4OH alone.

Surface Morphology

Though a bromine etch produces a Te rich layer and so native oxides on the HgCdTe surface, it can also remove a defective surface layer by etching it and is required in making some structures like mesas. Thus, a bromine etch may still be inevitable. We observed the $Hg_{0.7}Cd_{0.3}Te$ surface morphology and its changes after bromine-in-methanol (Br-MOH) etch and after the new surface treatment using atomic force microscopy (AFM). The results are shown in Fig. 5.

Figure 5a is the AFM view of the HgCdTe surface after polishing only. Mean height is 42Å and root mean square (rms) surface roughness is 17Å. Figure 5b is the view of the HgCdTe surface after it was etched with 1 vol. % Br-MeOH for 2.5 min. The surface became very rough and so the mean height and rms roughness increased to 115 and 41Å, respectively. This increase of surface roughness will result in the electrical instability of the passivation layer and will
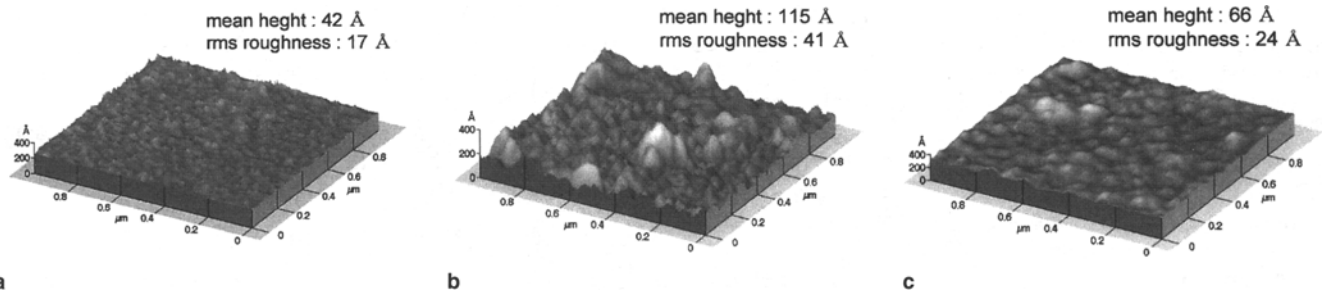
Fig. 5. AFM perspective views of Hg$_{0.7}$Cd$_{0.3}$Te surfaces (a) as polished, (b) etched with 1 vol.% Br-MeOH for 2.5 min, and (c) after treated with the procedure of chemical oxidation and removal of the oxide.

Table I. Summary of MIS Parameters

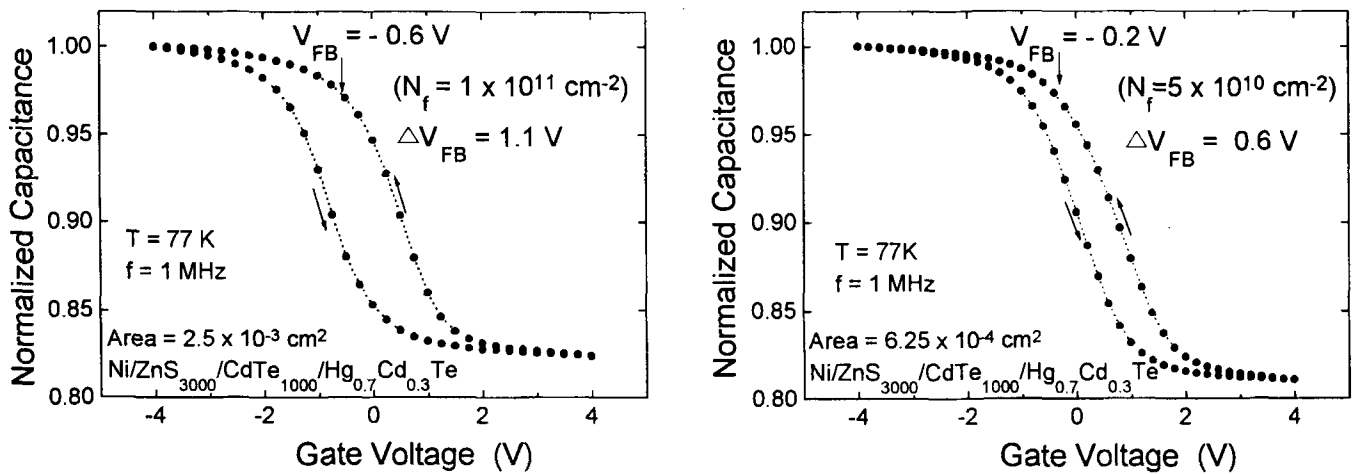| Sample	Br-MeOH Etch	Post-Etch Treatments	N_f (cm^{-2})	N_{SS} (cm^{-2})	Remarks
1	0.2 vol. %, 5 min	×	1×10^{11}	1.5×10^{11}	shown in Fig. 6a
2	0.5 vol. %, 4 min	×	1.6×10^{11}	1.5×10^{11}	
3	0.5 vol. %, 4 min	the new surface treatment	5×10^{10}	6.5×10^{10}	shown in Fig. 6b

Fig. 6. C-V curves of double layer MIS capacitors fabricated (a) without the new surface treatment method, and (b) with the new surface treatment method.

decrease the yield of HgCdTe devices.[9] The roughened HgCdTe surface can be made smooth with the new surface treatment. The result is shown in Fig. 5c. Mean height and rms roughness reduced to 66 and 24Å, respectively. Thus, the new surface treatment is expected to improve the electrical stability of the passivation layer.

MIS Capacitors

In order to examine the effects of the new surface treatment on the electrical properties of CdTe passivation, MIS capacitors with ZnS/CdTe passivation layer were fabricated and characterized. They were also measured at 77K with 1 MHz frequency. The measured C-V curves are shown in Fig. 6. Figure 6a is from the MIS capacitor fabricated only with Br-MeOH etch, and Fig. 6b is from the one fabricated with the new method. Both C-V curves show hysteresis which is thought to result from native oxide layers formed when the HgCdTe surfaces were ex-

posed to air.[10,11]

The hysteresis of C-V curves is directly related to slow surface states which are responsible for the high noise level of photodiodes. However, the hysteresis width in Fig. 6b is about half of that in Fig. 6a. The slow surface state densities (N_{SS}) determined from the hysteresis widths are 1.5×10^{11} cm^{-2} for Fig. 6a and 6.5×10^{10} cm^{-2} for Fig. 6b. Hence, the new surface treatment reduces the slow surface state density at the interface.

More important is the fixed charge density (N_f) which is responsible for the excessive dark currents of photodiodes. While the N_f value in the Fig. 6a is 1×10^{11} cm^{-2}, that value in Fig. 6b is 5×10^{10} cm^{-2} which is acceptable for high performance photodiodes. Thus, the new surface treatment can result in a near flatband condition. The MIS parameters are summarized in Table I.

The improvements of the C-V characteristics by the new surface treatment are more interesting consider-

ing that the fixed charge density and the surface roughness are expected to increase as the bromine concentration increases.[9] As shown in the Table I, the substrate in Fig. 6b was etched with a higher concentration of Br-MeOH than that in Fig. 6a. Nonetheless, it showed lower fixed charge and slow surface state densities. Thus, it can be said that the new surface treatment can reduce the bad effects of Br-MeOH etch on the HgCdTe surface.

The improved C-V characteristics of MIS capacitors resulting from the new surface treatment were reproducibly obtained in successive similar experiments. Without the new surface treatment, the C-V characteristics were not reproducible and depended on the Br-MeOH etching conditions such as the bromine concentration and the etch time. Even the substrate carrier concentrations determined from the C-V curves were often several times higher than expected when the HgCdTe wafer was not treated with the new surface treatment.

CONCLUSIONS

In this paper, a new simple surface treatment method was presented which is a kind of post-etch treatment composed of chemical oxidation of HgCdTe and removal of the oxide. Since strong HNO_3 is used, the new method can make the HgCdTe surface cleaner than conventional methods. Even though the HgCdTe surface is roughened by Br-MeOH etch, the surface can be made smooth with the new method. In applications to the MIS capacitors, the new surface treatment resulted in reproducible improvements in C-V characteristics such as low fixed charge and slow

surface state densities. These improvements are thought to result from two aspects. One is the surface smoothing function of the new surface treatment. The other is that the nonstoichiometric surface layer of the HgCdTe caused by Br-MeOH etch may be consumed by the chemical oxidation and then removed together with the oxide.

ACKNOWLEDGMENTS

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