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Surface modification of SiC semiconducting materials using fluorine gas for the formation of plating film with high adhesion

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ABSTRACT

The surface of SiC wafer was pretreated using sintering process. And different thickness of SiO_2 layer could be acquired. Decreasing the thickness of SiO_2 layer on SiC samples, the roughness is showing a tendency to increase. The surface of SiC wafer was fluorinated with F_2 and O_2 mixing gases at 25℃ for 1h. The adhesion strength of Ni metal deposited on the SiC substrate could be enhanced by the surface fluorination.

1. INTRODUCTION

As silicon carbide (SiC) has better electrical and thermal properties including band gap energy, breakdown field and thermal conductivity than Si as well as outstanding chemical stability, much research is underway to use it in the field of semiconductor for high temperature and high power environment [1-3]. The SiC is very high quality semiconductor, making it ideal for the production of such circuits, although other materials have been explored historically. Integrated circuits are very small, complex electrical components that have multiple metal interconnect layers coupled to a vast number of electrical elements within a very small unit of area. Each layer of an integrated circuit typically has a specific pattern of metal interconnects responsible. Copper or nickel is rapidly replacing aluminum in metal interconnects in the ultra-large scale integration (ULSI) technology [4-5]. Metals on SiC can be deposited by plasma vapor deposition (PVD), laser-induced reflow, chemical vapor deposition (CVD), electroless deposition, and electroplating [6-7]. The electroless deposition technique is especially appealing because of its low cost, inherent selectivity and ability to deposit high quality films on very thin seed layers [8]. However, the adhesion of the electrolessly deposited metal to the SiC surface to an effective pretreatment prior to the electroless metallization process is a necessary and essential step. The methods for the modification of silicon surfaces have included chemical etching [9], plasma immersion ion implantation [10], chemical vapor deposition [11], dry seeding via sputtering [12], plasma graft polymerization [13], etc. Among them, dilute HF (DHF)-based etching is widely used in semiconductor processing. However, the chemical stability of the DHF-etched SIC surface can be abruptly eliminated by a trace amount of metallic impurities, like Cu, Ag, Pd, and Au etc., present in HF-related etching solution [14].

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In this study, we report the effect of direct fluorination on the surface modification of SiC wafer and on the adhesion strength between SiC wafer and metal film prepared using electroless plating method.

2. EXPERIMENTAL DETAILS

2.1 Materials

SiC wafer having a thickness of about 1 mm and a diameter of 100 mm, were obtained as 4H-SiC from TANKEBLUE INC. To investigate the effects of SiO_2 layers on SiC samples about the adhesion of metal film, three sintering conditions were carried out as indicated in Table 1. From the XPS results, the thickness of SiO_2 layers was depended on the sintering conditions.

Table 1 Sample name and pretreatment conditions.

Sample name	Pretreatment conditions (sintering)	SiO_2 thickness (nm)*
SiC-A	1000℃, 1h, 45min	10
SiC-B	500℃, 24h, 0min	1
SiC-C	1000℃, 1h, 45min → 500℃, 1h, 45min	100

*SiO_2 thickness was evaluated from XPS results.

2.2 Surface fluorination

SiC wafers were sliced into square strips of about 10 mm x 10 mm in size. To remove the organic residues on the surface, the substrate was washed with ethanol. Details of the fluorination apparatus have been given in our previous paper [15, 16]. Fluorinated SiC wafers (noted as F-SiC) were prepared by direct fluorination using the gases mixed as 10 torr and 10 torr with F_2 and O_2 at 25℃ for 1h.

2.3 Electroless Ni plating

As the hydrophilic treatment, the samples were stirred in an aqueous solution of 2 wt% surfactant at 60℃ for 30min and dried in a 70℃ air chamber and washing with ion-exchanged water. Regarding the sensitizing process for electroless metal plating, the samples were immersed in an aqueous solution of 2 wt% tin(II) chloride dehydrate (Kanto Chemical Co. Inc.) and 1 vol.% hydrochloric acid (12M; Nacali Tesque Inc.) for 10min, followed by gentle rinsing with ion-exchanged water. For the activation process, sensitized SiC samples were immersed in an aqueous solution of 0.1 wt% palladium (II) chloride (Mitsuwa Chemical Co. Ltd.) and 0.5 vol.% hydrochloride acid (12M) for 2 min, followed by gentle rinsing with ion-exchanged water. The electroless plating bath was prepared using 20 g/dm^3 nickel (II) sulfate hexahydrate (Nacali Tesque Inc.), 30 g/dm^3 tri-sodium citrate dehydrate (Nacali Tesque Inc.), and sodium ammonium solution (Kanto Chemical Co. Inc.) as a pH adjuster. Then sodium phosphinate monohydrate (Nacali Tesque Inc.) was used as the reducing agent. The activated SiC samples were put into an electroless bath of 100ml, which was controlled at 60℃ and pH 9.0. Finally,

the substrate was rinsed carefully with ion-exchanged water and dried in a 70℃ air chamber.

2.4 Measurements

The chemical composition of SiC surface was determined by X-ray photoelectron spectroscopy (XPS, XPS-9010). All binding energies were referenced to the C 1s hydrocarbon peak at 284.5 eV. The topographies of sample surface were studied by atomic force microscopy (AFM), using a Nanoscope IIIa AFM from the Digital Instrument Inc. In each case, an area of 5 x 5 um square was scanned using the tapping mode. An arithmetic mean of the surface roughness (Ra) was calculated from the roughness profile determined by AFM. Static water contact angles of the samples were measured at 25℃ by the sessile drop method, using 3 uL water droplet in a telescope goniometer (Rame-Hart, model 100-00-(230), manufactured by the Rame-Hart, Inc. of Mountain Lakes, NJ). The telescope with a magnification power of 23x was equipped with a protractor of 1° graduation. For each sample, at least five measurements from different surface locations were averaged. Each angle reported was reliable to ±2° .

3. RESULTS and DISCUSSION

3.1 AFM images

Surface roughness (Ra) of untreated and fluorinated samples was measured using AFM analysis as shown in Fig.1. Pretreatment of samples affected the surface roughness (Ra). Especially, the roughness of SiC-B sample was 2.408nm higher than those of other samples. Decreasing the thickness of SiO_2 layer on SiC samples, the roughness is showing a tendency to increase. This tendency was almost same even after surface fluorination. Before and after surface fluorination, the surface roughness didn't changed. Namely, the surface fluorination never affects the surface roughness at this time. It needs to reconsider the fluorination conditions.

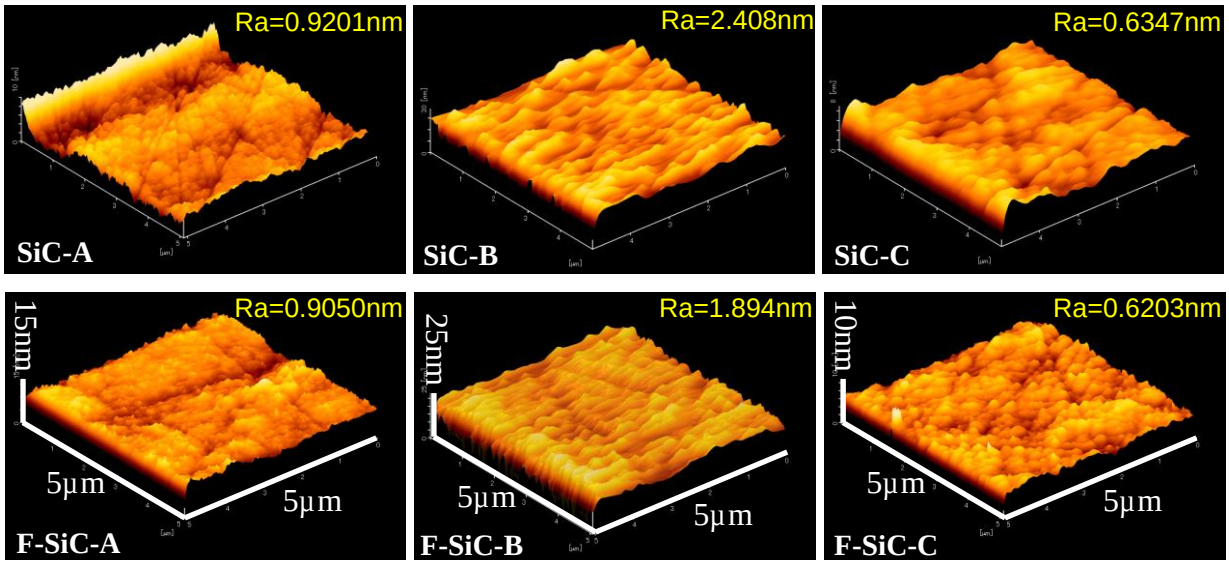


Fig.1 AFM images of untreated and fluorinated samples.

3.2 Contact angles

The water contact angles on the surface of each sample were shown in Fig. 2. As same as roughness results in Fig.1, the surface fluorination did not affect the hydrophilic properties on the SiC surface. Also the effect of pretreatment did not seen in the results of contact angle.

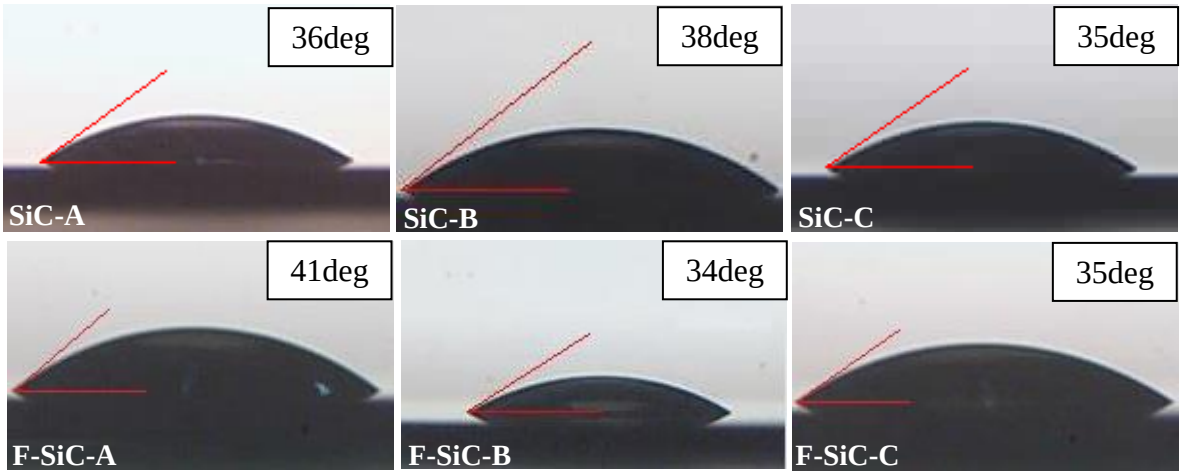


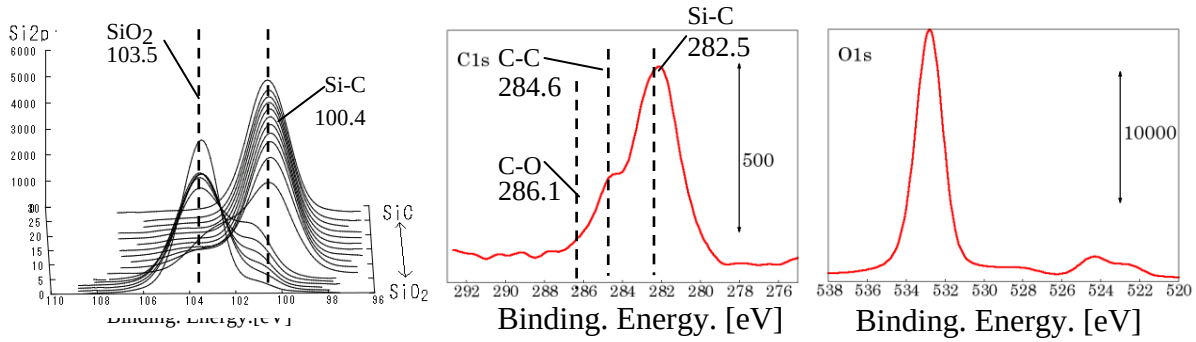
Fig.2 Contact angles with water of various samples.

3.3 XPS results

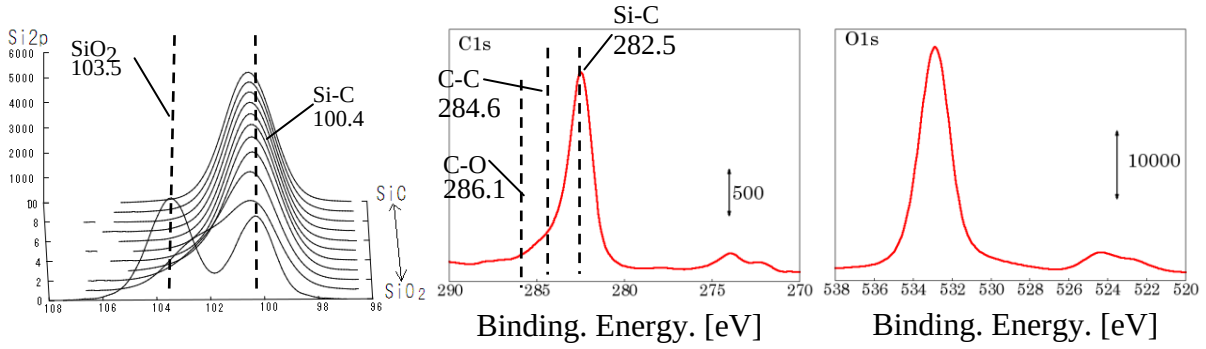
Figure 3 shows the XPS results of untreated samples. In case of (a) SiC-A sample, the thickness of SiO_2 layer was confirmed about 10nm using a Ar^+ ion etching. From the C1s result, SiC peak was detected at 282.4 eV. In case of (b) SiC-B sample, the thickness of SiO_2 layer was about 1nm. And both SiO_2 and SiC was existed on the surface. In case of (c) SiC-C sample, the thickness of SiO_2 layer was about 100nm. From the C1s result, there was not detected any Si-C bonds. It means that thick SiO_2 layer was created on the surface.

Figure 4 shows the XPS results of fluorinated samples. Comparing with untreated thing, fluoride peaks were detected on the F1s spectra. In detail, Si-F peak at 685.6 eV, C-F peak at 684.5 eV and O-F peak at 687.7 eV were confirmed in XPS results. It means that the SiO2 and SiC change into SiOF2 or SiCFx after fluorination.

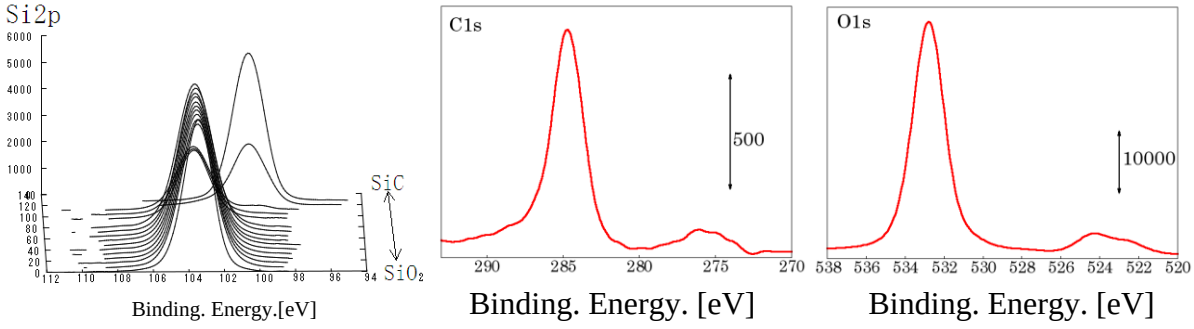
Table 2 shows the atomic percent of fluorinated samples in Fig.4. Among various samples, the amounts of fluoride in F-SiC-B were larger than other samples. Namely, the surface of F-SiC-B sample can be easily reacted with F_2 gas.



(a) SiC-A

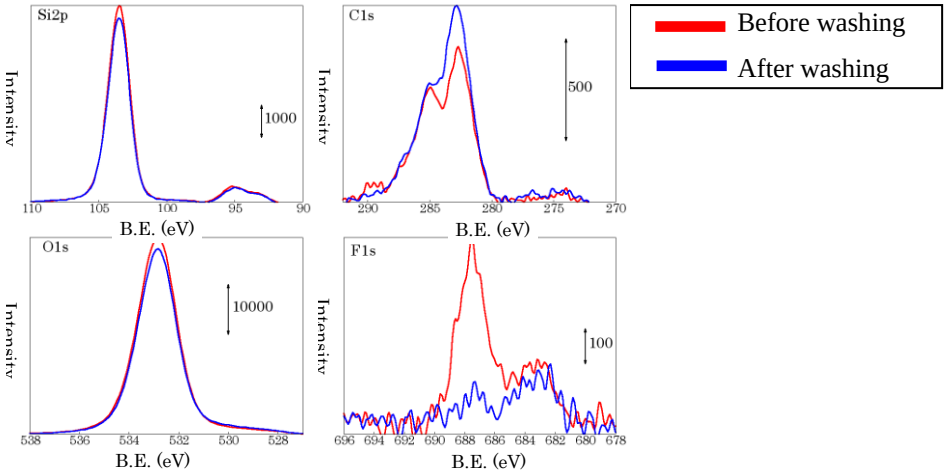


(b) SiC-B

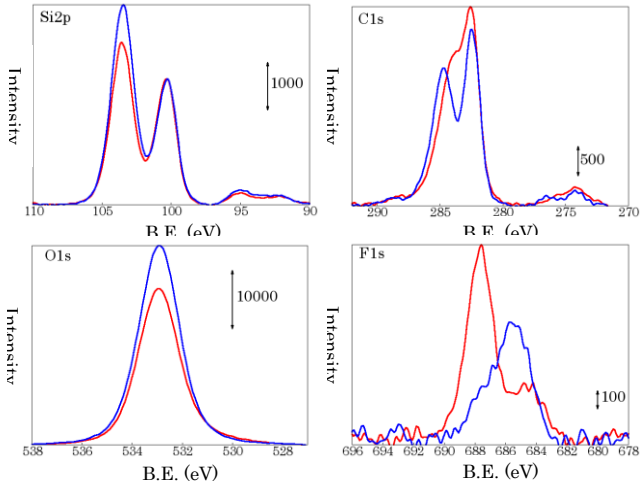


(c) SiC-B

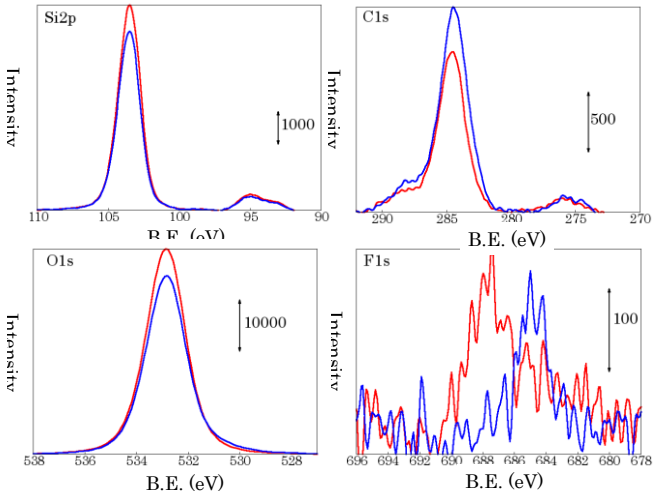
Fig.3 XPS results of untreated samples.



(a) F-SiC-A



(b) F-SiC-B



(c) F-SiC-C

Fig.4 XPS results of fluorinated samples.

Table 2. Atomic percent of fluorinated sample.

Sample name	Water wash	Si 2p3/2	C 1s	O 1s	F 1s
F-SiC-A	No	28.98	6.888	63.07	1.064
	Yes	28.67	8.346	62.41	0.575
F-SiC-B	No	28.57	22.70	46.85	1.877
	Yes	28.78	18.54	51.55	1.130
F-SiC-C	No	29.36	8.273	61.69	0.678
	Yes	27.91	11.66	59.98	0.454

3.4 Adhesion test

By using an electroless method, the Ni plating was carried out on the SiC surface. In case of untreated samples, the peeling of Ni film was occurred in the electroless process. And the Ni film on the SiC samples did not uniform as shown in Fig. 5. On the other hand, in case of fluorinated samples, the Ni film can be plated uniformly on the surface. The adhesion strength between the Ni metal layer and various SiC samples was investigated using the cross-cut tape test. Comparing with untreated samples, the fluorinated samples indicated the strong adhesion of the metal to the substrate.

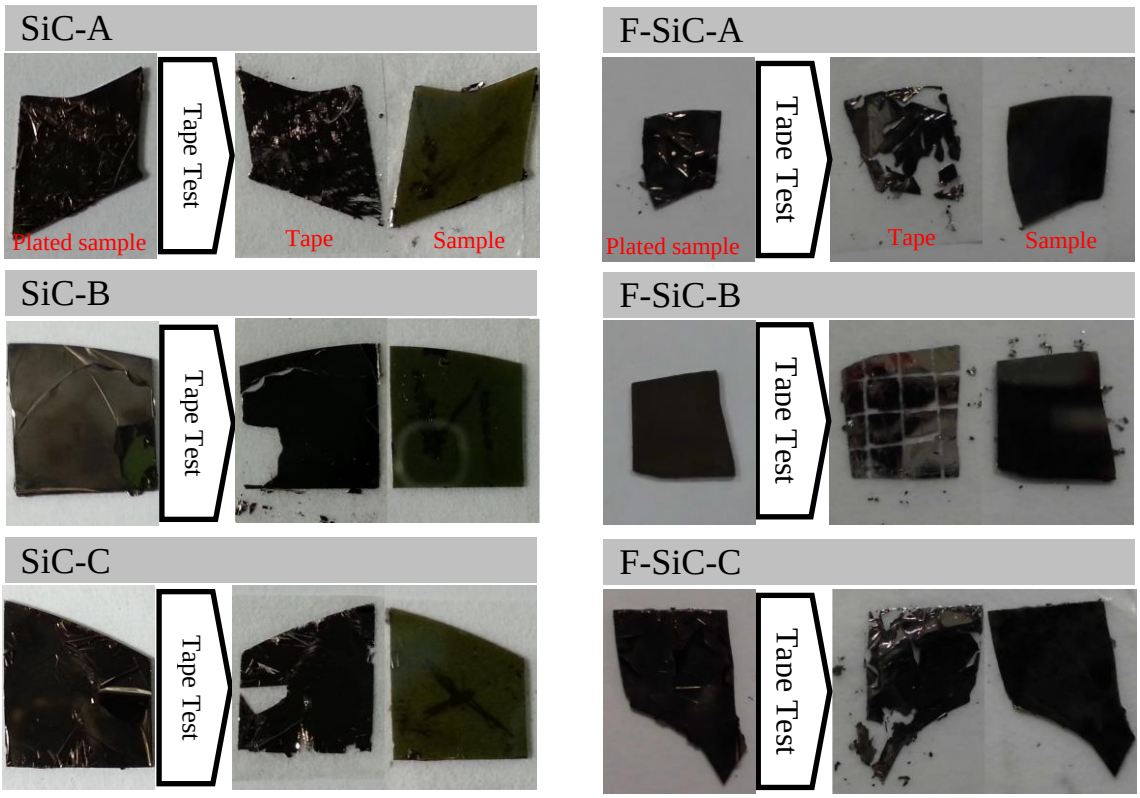


Fig.5 Adhesion strength of various SiC samples using tape test.

Especially, the F-SiC-B sample was superior to other samples. However, there are still remained the metal traces on the peel-off tapes in all samples. By the way, the adhesion strength between fluorinated SiC sample and metal film could be enhanced by an anchor effect.

4. CONCLISIONS

By using a pretreatment sintering process, the thickness of SiO2 layer on the SiC samples could be adjusted as 1 to 100 nm. Decreasing the thickness of SiO_2 layer on SiC samples, the roughness is showing a tendency to increase. This tendency was almost same even after surface fluorination. The surface of SiC wafer was treated using direct fluorination with F_2 and O_2 mixing gas. Through the tape test, the adhesion

strength between fluorinated SiC sample and metal film could be enhanced by an anchor effect.

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