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Effects of Sulfurization on the Properties of 4H-SiC Schottky Contacts

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Abstract. This paper reports on the effect of a sulfurization thermal process of the silicon carbide surface on the properties of Ni/4H-SiC Schottky barrier. In particular, the incorporation of sulfur (S) in the 4H-SiC near-surface region was observed at the process performed at 800 °C, without any significant effect on the surface morphology. On the other hand, Ni/4H-SiC Schottky contacts fabricated on the sulfurized 4H-SiC surface showed a 0.3 eV reduction of the average barrier height with a narrower distribution, with respect to the untreated sample. These results were explained by an increase of the 4H-SiC electron affinity after sulfurization, and a Fermi level pinning effect.

Introduction

Controlling the electrical properties of metal/SiC interfaces is a challenging issue, because of the numerous implications in Schottky barrier diodes technology [1]. In particular, tailored barrier characteristics and reduced power losses are among the main goals in this technology [2]. In this context, over the years, metals with different work function (Φ_m) have been employed for obtaining the desired metal/4H-SiC Schottky Barrier Height (SBH), due to the linear dependence of the SBH on the metal work function Φ_m often observed in SiC [3]. However, the occurrence of Fermi-level-pinning (FLP) may reduce the dependence of the SBH on the metal work function Φ_m [4]. Hence, several surface/interface processes have been also investigated to exploit this effect. For example, plasma treatments in combination with thermal annealings have been used to control the reduction of the SBH in 4H-SiC and to achieve more uniform current-voltage characteristics with acceptable leakage current values [5-7]. In particular, using a CF_4 plasma treatment, a significant barrier lowering was observed, which could be completely recovered after appropriate silicidation annealings leading to the consumption of a 4H-SiC surface layer [8]. More recently, the insertion of an ultrathin a-SiC:H interlayer below the metal was also used to modify the SBH in 4H-SiC Schottky diodes, using the strong FLP effect occurring in the presence of the defect-rich amorphous layer [9]. Finally, also ion-implantation of foreign species in 4H-SiC layer was used to modify the SBH properties, either by near-surface dopant deactivation [10] or by the creation of electrically active interface defects [11].

In this context, since almost two decades sulfur (S) is known to act as a deep donor of 4H-SiC [12], and the electrical activation of S double donors introduced in 4H-SiC by ion implantation has been recently object of interest for transistors applications [13]. Besides ion-implantation, also thermal treatments in S-atmosphere of ultra-thin deposited Mo films on 4H-SiC surface have been recently considered for developing novel device concepts based on atomically thin molybdenum disulfide (MoS_2) heterojunctions with SiC [14]. However, the effects of these sulfurization treatments on the electrical properties of 4H-SiC surface are still unclear and need to be investigated.

In this paper, the effects of a sulfurization treatment of the 4H-SiC surface were evaluated by detailed chemical, morphological and electrical analyses of Ni/4H-SiC Schottky contacts. In particular, a chemical analysis demonstrated an incorporation of sulfur (S) in the 4H-SiC surface treated at 800 °C. The Ni/4H-SiC Schottky contacts fabricated on the "sulfurized" 4H-SiC surface exhibited a 0.3 eV reduction of the Schottky barrier with respect to the "untreated" sample (not subjected to sulfurization). This effect was explained by a decrease of the electron affinity and Fermi level pinning effect induced by the sulfurization.

Experimental

In this experimental investigation, we used silicon carbide (4H-SiC) samples, consisting of an n-type epitaxial layer ($N_D=1\times10^{16}$ cm^{-3}) grown onto a n^+ doped substrate.

The surface of the 4H-SiC samples was exposed to a "sulfurization" treatment in a two-heating zones quartz tube. This procedure is described in more detail in the next section.

The chemical impact of the sulfurization was evaluated by X-ray photoelectron spectroscopy (XPS) analyses performed by using an Escalab Xi+ equipment by Thermo Fisher with a monochromatic Al K X-ray source. Spectra were recorded with 0.1eV steps for the main components of the system like Si 2p (102eV), C 1s (285eV) O 1s (532eV) and sulfur 2p (162eV). Since the expected small peak of low sulfur content, the sensitivity was raised by applying: (i) a high pass energy (60eV) resulting in a resolution of 1.1eV; (ii) a long measurement time (2.5 sec / point); (iii) a large X-ray spot (950µm) to provide high count rate.

The morphology and the surface potential of 4H-SiC surfaces were monitored by Atomic Force Microscopy (AFM) and Kelvin Probe Force Microscopy (KPFM) carried out in Peak Force Tapping Mode with a Dimension Icon system by Bruker. For KPFM measurements, silicon tips with a nominal radius of 5 nm and a spring constant of 0.8 N/m supported on a silicon nitride cantilever were employed.

The effect of the sulfurization on the electrical properties of Ni/4H-SiC Schottky contacts was studied by means of test Schottky diodes. In particular, first a back-side Ohmic contact was fabricated by sputtering 100 nm-thick Ni film, followed by a rapid thermal annealing at 950 °C in N_2. Then, the sample surface was subjected to the sulfurization process identified as the most suitable for S incorporation (800 °C). Finally, the front-side circular Schottky contacts (active area of 10^{-4} cm^2) were formed by 100 nm-thick Ni layer, followed by a thermal annealing at 400 °C.

The current voltage (I-V) electrical characterization of these diodes was carried out on a set of equivalent devices, using a probe station equipped with a parameter analyzer.

Results and Discussion

A schematic illustration of the experimental set-up used for the sulfurization processes is depicted in Fig. 1a. It consists in a two-heating zones quartz tube, containing a crucible filled with Sulphur (S) powder. The crucible is placed in the lower-temperature zone kept at 225 °C, whereas the 4H-SiC sample is placed in the higher-temperature zone (which could be varied in the range 800-1000°C). Argon (Ar) was used as carrier gas at flow rate of 50 sccm. The sulfurization time was 90 minutes, thus producing the evaporation of about 1 g of S from the crucible.

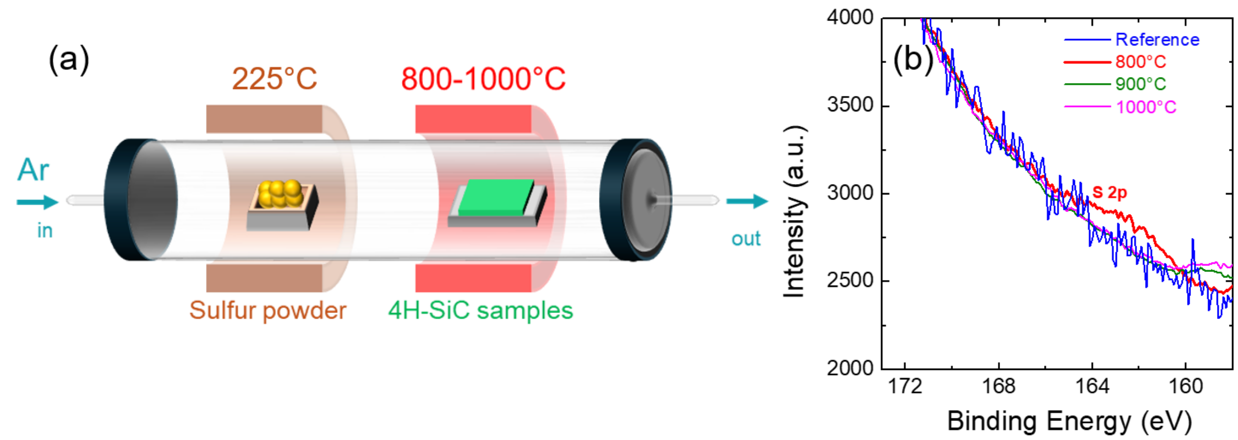

Fig. 1. (a) Schematic of the experimental set-up of the quartz tube furnace used for the sulfurization process of SiC surface; (b) S2p peak of XPS spectra obtained on 4H-SiC samples subjected to sulfurization at 800°C, 900°C and 1000°C. The spectrum of an untreated sample (reference) is shown for comparison.

The 4H-SiC samples were subjected to sulfurization at three different temperatures, i.e. 800, 900 and 1000 °C. After these processes, the sulfurized samples were studied by XPS analyses to verify the presence of sulfur (S) in the near-surface region. An untreated 4H-SiC sample was analyzed as a reference. The corresponding XPS spectra are reported in Fig.1b. In particular, the acquired XPS spectra showed a visible presence of sulfur only after the process carried out at 800 °C. Here, the expected S 2p doublet is broadened onto a wide peak visible at 162.5 eV. The background shape originates from the proximity of the plasmon satellites of the Si 2s. Interestingly, the binding energy of this peak is consistent with S atoms bonded to the topmost Si atoms of the SiC lattice, as recently reported in Ref. [15]. Since the S 2p peak is a low intensity peak with noisy condition on top of a bended background, only an estimate can be given for its quantity. Considering the low diffusion coefficients of foreign species in SiC, it is reasonable to assume the sulfur being distributed within a depth of 1nm. Hence, by assuming a homogeneous distribution of sulfur in such a thin surface region, a concentration in the range of 0.6-1.6 at. % could be estimated. It must be noted that the spectra detected on the 900 °C and 1000 °C annealed samples showed a sulfur peak at the noise level, i.e. 10 times lower sulfur concentrations (if any) than that of 800 °C annealed sample. Hence, we speculate that, while at low temperatures sulfur is incorporated in the near-surface region of SiC, with increasing temperature (> 800°C) the competitive effect of its evaporation becomes dominant, and no sulfur is observed by our chemical analysis.
Figs. 2a and 2b report the AFM surface morphology of 4H-SiC before and after the sulfurization process carried out at 800 °C, respectively. In particular, the typical steps associated to the 4°-off-cut angle of 4H-SiC epilayers are visible. More interestingly, the surface roughness of the epilayer is almost unaffected by the sulfurization, since very similar root mean square (RMS) values are found, i.e., 0.15 nm before and 0.17 nm after the process.

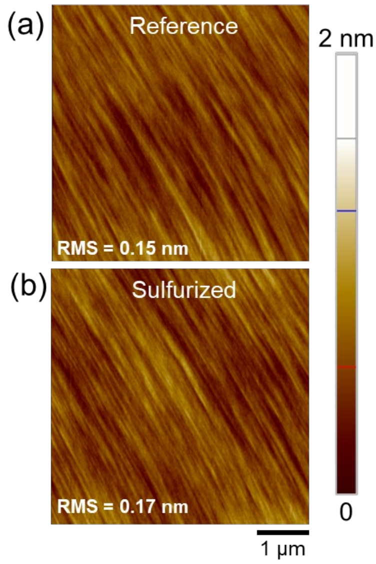

Fig. 2. Surface morphology of 4H-SiC samples before (a) and after (b) the sulfurization process at 800 °C.

To monitor the effects of the sulfurization on the electrical properties of the 4H-SiC surface, first Ni/4H-SiC Schottky didoes were fabricated and characterized by I-V measurements.
Fig. 3a shows a collection of different forward I-V curves of Ni/4H-SiC Schottky diodes fabricated on the reference (untreated) and the sulfurized (800 °C) sample.

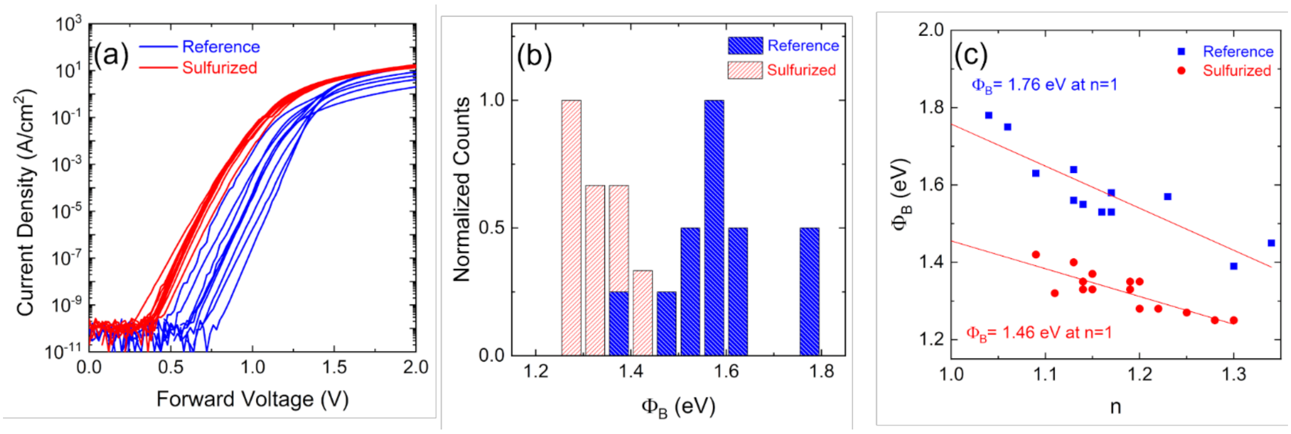

Fig. 3. (a) Forward I-V curves of Ni/4H-SiC Schottky diodes fabricated on the untreated 4H-SiC sample (reference) and on the sample subjected to sulfurization at 800°C (sulfurized). (b) Statistical distributions of the Schottky barrier height values determined in the reference and in the sulfurized diodes. (c) Plot of the Schottky barrier Φ_B as a function of the ideality factor n determined in the Ni/4H-SiC Schottky diodes fabricated on reference and on a sulfurized (800 °C) sample. The continuous lines are a linear fit of the experimental data, from which the ideal values of the Schottky barrier height can be extrapolated (at n=1).

As can be seen, the I-V curves of the sulfurized samples (800 °C) are shifted towards lower forward voltage values, thus indicating a lowering of the SBH. In addition, the measured I-V curves appear more reproducible with respect to those of the reference Ni/4H-SiC diodes, thus suggesting that a more uniform distribution of the barrier is occurring. This is well visible in Fig. 3b, showing the statistical distributions of the SBH values in the two cases. As can be seen, while the distribution of the SBH values of the reference diodes is peaked at 1.58 eV, the average of the SBH distribution in the sulfurized sample is 1.32 eV, i.e. with a lowering of about 0.26 eV with respect to the reference. Moreover, the SBH distribution of the sulfurized diodes appears narrower with respect to the reference, as expected by the forward I-V curves reported in Fig. 3a.

Finally, Fig. 3c reports the experimental values of the SBH as a function of the ideality factor n, for the reference and the sulfurized sample. Interestingly, a linear correlation between these two parameters (Φ_B and n) is observed, which is a typical macroscopic signature of the barrier inhomogeneity at a microscopic level [5,16]. From this plot, it was possible to extrapolate the "ideal values" (at n=1) of homogeneous barrier, i.e. 1.76 eV for the reference sample and 1.46 eV for the sulfurized one. The different slope of the Φ_B vs n plots reflects the different degree of homogeneity of the barrier [17], and it is fully coherent with the narrower SBH distribution of the barriers observed in the sulfurized sample (Fig. 3b).
Finally, the get further insights on the effect of S incorporation on the electrical properties of 4H-SiC surface, a surface potential mapping of the samples was carried out using KPFM. As a reference value of the surface potential, a pattern of gold (Au) stripes was created on the sample surface by optical lithography and lift off.
Figs. 4a and 4b report the two-dimensional surface potential maps collected on regions including the Au stripe and the bare 4H-SiC surface, for the reference and the sulfurized sample, respectively. The surface potential line-profiles across the two regions are also reported in the inserts of the two figures, showing a reduced surface potential difference with respect to Au in the sulfurized 4H-SiC surface (~0.7 V) with respect to the untreated one (~1 V). To obtain statistically relevant information on the entire scanned areas, the histograms of surface potential values extracted from these KPFM maps are also reported in Fig. 4c and 4d. The two distributions include a peak associated to Au surface and a second peak associated to bare SiC surface (reference and sulfurized). A Gaussian fit of these distributions enables to better quantify the shift of the 4H-SiC surface potential with respect to the reference Au stripe. From this analysis, a 0.3 V increase of the surface potential of sulfurized 4H-SiC with respect to the untreated 4H-SiC surface could be estimated, which corresponds to an increase of the 4H-SiC electron affinity induced by the sulfurization process.

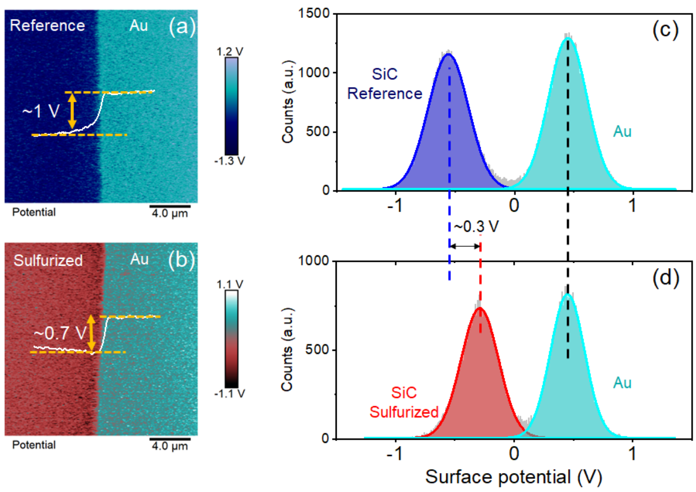

Fig. 4. (a) Surface potential maps of the Au stripe (cyan region) compared to (a) the untreated SiC (blue region) and (b) to the sulfurized SiC (red region). Surface potential line profiles across the Au coated and bare SiC regions are reported as inserts of the two maps (c) Histograms of the surface potential values extracted from the KPFM maps on (c) untreated SiC and (d) after sulfurization. Here, a reduction of the surface potential of ~0.3 V is observed on the sulfurized SiC.

The experimentally observed scenario is graphically depicted in Fig. 5, which reports the schematic band diagram of the metal/4H-SiC system before and after the sulfurization process. As can be seen, a reduction of the 4H-SiC electron affinity and Fermi level pinning at the surface induce a lowering of the Schottky barrier height in the sulfurized sample.

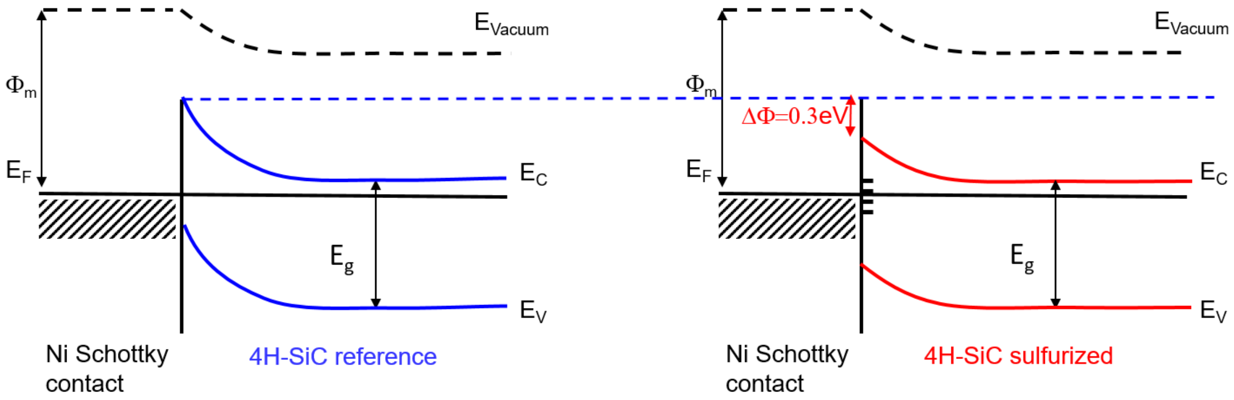

Fig. 5. Schematic band diagram of the Ni/4H-SiC band diagram before and after sulfurization process at 800 °C, showing the barrier lowering of 0.3 eV.

It is worth mentioning that capacitance-voltage analyses of the diodes, not reported here, did not reveal any variation of the doping level upon sulfurization process [18].

Summary

In summary, the effects of a sulfurization of the 4H-SiC surface on Ni/4H-SiC Schottky barrier was studied by the cross-correlation of several chemical, morphological and electrical analyses.
In particular, the incorporation of sulfur (S) in the 4H-SiC surface occurs after sulfurization at 800 °C, without causing any significant degradation on the 4H-SiC surface morphology. On the other hand, Ni/4H-SiC Schottky contacts fabricated on the sulfurized 4H-SiC surface exhibit a 0.3 eV reduction of the average barrier height with a narrower distribution, with respect to the untreated sample. These results, explained by an increase of the 4H-SiC electron affinity after sulfurization, and a Fermi level pinning effect, can be useful for 4H-SiC power device technology and for the integration of S-based layered materials (e.g. MoS_2) on SiC surfaces for novel devices concepts.

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