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Effects of H-Termination of Si(100) Surfaces on Electrical Characteristics of Metal/Silicon Interfaces

S. Zaima, J. Kojima, M. Hayashi, H. Ikeda, H. Iwano and Y. Yasuda

Department of Crystalline Materials Science,
School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Effects of H-termination on electrical characteristics of Hf/Si(100) interfaces have been examined. H-terminated surfaces are very stable for the adsorption of oxygen. Effective dielectric layer thicknesses of H-terminated Hf/p-Si Schottky interfaces are 1/4-1/3 times as small as those of non-terminated ones and the ideality factors in current-voltage characteristics are very close to unity. It can be concluded that the H-termination is markedly effective to improve electrical characteristics of Hf/p-Si interfaces.

1. INTRODUCTION

The formation and control of metal-semiconductor interfaces have attracted considerable attention because of the technological and scientific importance. Especially, the lowering of ohmic contact resistance has become essential to realize ultra-large scale integrated circuits (ULSI's) with decreasing device dimensions. Transition metals and their silicides are one of the candidates as materials with very low contact resistivities for future ULSI's. We have studied electrical properties and interfacial reactions of transition-metal/silicon contacts and found very low contact resistivities for Zr/ and Hf/n^+-Si(100) systems.[1] However, the contact resistivities for p^+-Si are larger than those for n^+-Si and the current-voltage (I-V) characteristics of p-Si Schottky diodes are very far from idealistic I-V characteristics.[1] One of possible explanations for these phenomena is effects of native oxide of Si. In addition, the presence of native oxide on Si surfaces promotes silicidation reaction even at room temperature.[2] Therefore, the development of surface cleaning and passivation processes is essential to form ohmic contacts with low resistivity and high reliability, and also to understand the factors dominating electrical characteristics.

Recently, H-termination of Si surfaces is studied extensively to control the formation of native oxide, and it is reported that the termination of dangling bonds with H atoms makes Si surfaces passive against the oxygen adsorption even in the atmosphere.[3] In the present paper, we report effects of H-termination of Si(100) on electrical characteristics of Hf/Si(100) interfaces. A marked improvement of the electrical characteristics due to the H-termination has been found.

2. EXPERIMENTAL

Substrates used for Schottky diodes were n- and p-Si(100) with resistivities of 1-3 and 0.5-0.7 Ωcm, respectively. Si wafers were chemically cleaned and dipped in a diluted HF solution ($HF:H_2O=1:50$) to remove thin SiO_2 layers and rinsed in flowing de-ionized (DI) water before setting in an ultra high vacuum (UHV) chamber. Si wafers were rinsed in DI water for 10 min and 2-5 sec for obtaining conventionally treated and H-terminated Si(100) surfaces, respectively. The surfaces treated with these procedures were examined by high-resolution electron energy loss spectroscopy (HREELS) and x-ray photoelectron spectroscopy (XPS) using MgKα radiation.

The chemically cleaned Si wafers were loaded into a vacuum evaporation chamber, whose base pressure was less than 5×10^{-10} Torr. Hafnium films were deposited by an electron-beam evaporator. After the evaporation, the samples were successively annealed at 460 and 580°C for 30 min in the evaporation chamber and then the films were patterned to form measurement devices. Ohmic contacts with substrates were formed by Al electrodes through heavily-doped diffused layers on the backside.

Current-voltage (I-V) characteristics of Schottky diodes were measured in the temperature range of 77 to 300 K. Schottky barrier heights were

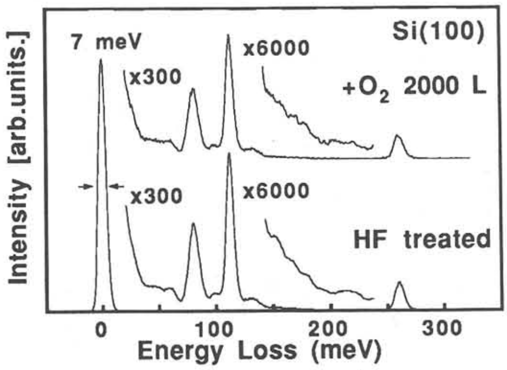

Figure 1. HREELS spectra from H-terminated Si(100) surfaces without and with 2000-L-O_2 exposure at room temperature.

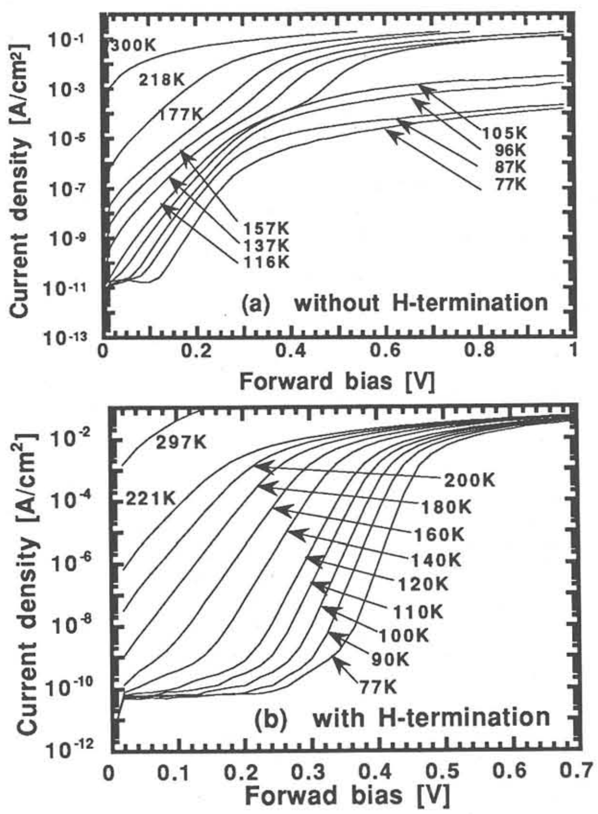

Figure 2. Current-voltage characteristics of as-deposited Hf/p-Si diodes (a) without and (b) with H termination.

determined from the temperature dependence of I-V characteristics and also capacitance-voltage (C-V) characteristics at 1MHz. Furthermore, deep levels at the Hf/Si interfaces were examined by deep level transient spectroscopy (DLTS).

3. RESULTS AND DISCUSSIONS

Figure 1 shows HREELS spectra of the H-terminated surface as-treated and exposed to 2000 L of O_2. Energy loss peaks of dihydride species (Si-2H) are clearly observed at 61, 78, 112 and 258.5 meV. This fact means that dangling bonds are bound to hydrogen atoms on the H-terminated surface. After exposing the surface to 2000-L-O_2, the spectrum hardly changes as seen in Fig. 1. Therefore, the H-terminated surface is very stable for O_2 exposure, although there exist peaks due to a very small amount of hydrocarbon.

Figure 2 shows I-V characteristics in the temperature range of 77 to 300 K for as-deposited Hf/p-Si diodes on the surface (a) without and (b) with H-termination. In the case of the diode without H-termination, the I-V characteristics are governed not only by thermionic emission current but also by other kinds of conduction current. One of the other mechanisms is considered to be the multi-step tunneling emission, in which the tunneling current flows through interfacial traps.[4] In the H-terminated case, on the other hand, the I-V characteristics are apparently governed by only the thermionic emission current.

The ideality factor n is defined as[5]

$$n \equiv \frac{q}{kT}\frac{\partial V}{\partial(\ln J)} ,$$

where J is the current density, k the Boltzmann constant, T the measurement temperature, q the electric charge, and V the bias voltage, respectively. The relationship between the ideality factor n and the bias voltage in the as-deposited diodes is shown in Fig. 3. In the case of the H-terminated sample, it is obvious that the n-value nearly equals unity in the wide bias range, in contrast to the sample without H-termination. Furthermore, the density of a trap observed by DLTS, with an energy of E_c-E_t=0.6 eV, is estimated to be in the order of 10^{12}-10^{13} cm^{-3} in the as-deposited Hf/p-Si diodes with H-termination. In the non-terminated diodes, DLTS spectra cannot be measured because of their very large reverse current. These results clearly indicate that the H-termination is effective to form an ideal metal/Si interface.

The Schottky barrier heights and n-values are

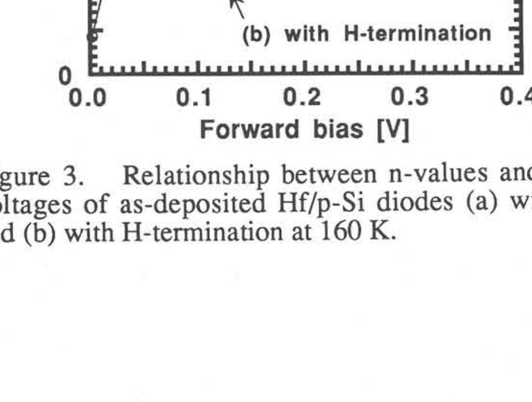

Figure 3. Relationship between n-values and bias voltages of as-deposited Hf/p-Si diodes (a) without and (b) with H-termination at 160 K.

Table 1. Schottky barrier heights ϕ_{Bp}, n-values and effective SiO_2-conversion thicknesses d_{ox} of dielectric layers, obtained from I-V and C-V characteristics of Hf/p-Si diodes with and without H termination.

Annealing Temperature	from I-V characteristics: H-terminated ϕ_{Bp} (eV)	H-terminated n value	non-terminated ϕ_{Bp} (eV)	non-terminated n value
as-deposited	0.56	1.10	-	1.80
460°C	0.53	1.12	0.50	1.38
580°C	0.51	1.10	0.51	1.17

Annealing Temperature	from C-V characteristics: H-terminated ϕ_{Bp} (eV)	H-terminated d_{ox} (A)	non-terminated ϕ_{Bp} (eV)	non-terminated d_{ox} (A)
as-deposited	0.69	1.6	-	-
460°C	0.75	2.6	(1.76)	11
580°C	0.74	2.8	(1.67)	9.5

summarized in Table 1. The characteristic features for the diodes without H-termination are that anomalous large barrier heights are obtained from C-V characteristics and also that the n-values from I-V are much larger than unity, which can be explained by the existence of a dielectric layer at the interface.[6] In Table 1, the effective SiO_2-conversion thicknesses d_{ox} of dielectric layers, estimated from the barrier heights of Hf/n-Si, are also listed. In the H-terminated diodes, on the other hand, the difference between the barrier heights from I-V and C-V becomes very small and n-values close to unity are also obtained. The values of d_{ox} in the H-terminated diodes are 1/4-1/3 times as small as those in the non-terminated ones. The origin of dielectric layers is not clear yet. However, this result suggests that native oxide or oxygen on the surface play an important role for the formation of non-ideal metal/Si interfaces.

Figure 4 shows XPS spectra of as-deposited samples of 35-Å-thick Hf films on Si(100) without and with H-termination. In the non-terminated sample, there observe peaks corresponding to hafnium oxides, which are indicated by arrows in Fig. 4. On the other hand, the peaks of the oxides are hardly observed for the H-terminated sample. It is considered that the oxide peaks observed in Fig. 4(a) result from the reduction of native oxide by Hf or the reaction with oxygen adsorbed on the surface.

The effect of H-termination is to prevent the oxygen adsorption on the Si surface. However, we should take account of the interaction with impurity atoms such as B, because the influence of dielectric layers hardly observed for n-Si diodes.[1] As reported in our previous paper,[7] the silicidation reaction is promoted by the reaction of Hf with native oxide. Therefore, the H-termination would be also effective

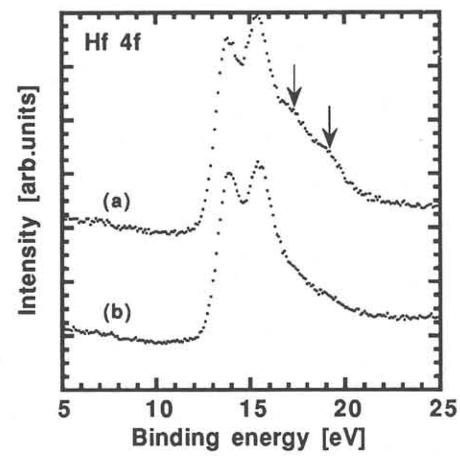

Figure 4. XPS spectra of Hf4f from as-deposited samples (a) without and (b) with H-termination. Arrows indicate peaks from hafnium oxide.

for suppression of the interfacial reactions.

4. CONCLUSIONS

The electrical characteristics of H-terminated Hf/p-Si(100) interfaces have been examined. The H-terminated Si(100) surface is very stable for oxygen adsorption. From I-V and C-V characteristics, it can be concluded that Hf/p-Si diodes with H-termination have an idealistic interface compared with those without H-termination. The effective dielectric layer thicknesses in the H-terminated diodes are 1/4-1/3 times smaller than those in the non-terminated ones and the n-values of the diodes are close to unity. The XPS peaks of hafnium oxide are hardly observed for the H-terminated case. The reason for the improvement of these electrical properties is that the amount of absorbed oxygen or the thickness of native oxide on the Si surface is reduced in consequence of the H-termination of dangling bonds. The H-termination is markedly effective to control and improve the metal/Si interfacial properties.

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