Formation and electrical properties of Hf Si_2 grown thermally from evaporated Hf and Si films

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2 MeV $^4He^+$ backscattering spectrometry and x-ray diffraction have been used to study Hf Si_2 formed by thermal annealing of a Hf Si film on evaporated Si (Si^e) at temperatures between 575 and 650 °C. A laterally uniform layer of Hf Si_2 forms and its thickness is proportional to the square root of time at a fixed temperature. The activation energy of this reaction is found to be 3.5 ± 0.3 eV. This transport-limited process differs from that observed on single crystal Si, where Hf Si_2 forms at temperatures above 700 °C by a process believed to be nucleation controlled. Four-point probe measurements of resistivity and Hall coefficient at room temperature on samples with both Hf Si and Hf Si_2 were used to determine that both Hf Si and Hf Si_2 are electron conductors. For Hf Si_2, the electron concentration is $2.9 \pm 0.2 \times 10^{21}$ cm^{-3} and the mobility is 36 ± 4 cm^2/Vs, giving a resistivity of 60 ± 3 $\mu\Omega$ cm. Schottky barrier diodes formed either by reacting a Hf film deposited directly on ⟨111⟩ Si or by reacting a Hf film with Si^e in a ⟨111⟩ Si/Hf/Si^e/Hf configuration at temperatures above 600 °C were prepared. The Schottky barrier height of Hf Si_2 on *n*-type ⟨111⟩ Si as evaluated from forward and reverse I–V characteristics is 0.54 ± 0.01 eV in both cases.

I. INTRODUCTION

Transition metal silicides have been used extensively as Ohmic contacts or interconnections in the manufacture of integrated circuits. Considerable efforts have been devoted to the study of the formation of metal silicides by solid-phase reaction.[1,2] When a thin Hf film begins to react with a single crystal Si substrate (Si^c) above 550 °C, it is found that Hf Si grows in a layer-by-layer fashion.[3] The formation of Hf Si is a diffusion-controlled process with an activation energy of 2.5 eV. Hf Si is stable on Si^c up to about 700–750 °C. Above that Hf Si transforms almost abruptly to Hf Si_2.[3,4] This transformation from Hf Si to Hf Si_2 is characterized by a rapid growth of Hf Si_2 throughout the whole Hf Si layer. In other words, the formation of Hf Si_2 from Si^c is a nucleation-controlled process. Hf Si_2 is the only refractory metal disilicide whose growth from Si^c is nucleation controlled. Similar phenomena have been observed in the formation of PdSi, $NiSi_2$, and $CoSi_2$ on Si^c.[1,4] However, recent investigations showed that $NiSi_2$ and $CoSi_2$ grow in a uniform layer-by-layer manner if Si^e is used instead of Si^c.[5–8] The layer-by-layer formation process takes place at lower temperatures than those required for the formation of the silicide on Si^c, which has been attributed to the elevated free energy of Si^e. It is therefore of interest to determine if the same phenomenon applies to other silicides whose growth kinetics on Si^c are nucleation controlled.

In the present work, we study the formation of Hf Si_2 from Si^e. We find that Hf Si_2 grows in a uniform layer-by-layer manner from Si^e and Hf Si at temperatures above 575 °C, in contrast with the formation of Hf Si_2 from Si^c. The Schottky barrier heights of Hf Si_2 on *n*-type ⟨111⟩ Si formed by reacting Hf with Si^c and Si^e are compared.

II. EXPERIMENTAL PROCEDURE

Three different sets of samples were prepared. The first set was used to study the growth kinetics of Hf Si_2 from Si^e and Hf Si. Commercially prepared and polished *p*-type ⟨100⟩ Si wafers of resistivity 1.5–2.5 Ωcm were used. Prior to loading into an oil-free e-beam evaporation system, the wafers were first oxidized slightly in an oxygen plasma for 10 min and then rinsed in deionized water followed by etching in a 10% HF solution for 5 min. Hf films of 2900 Å and Si films of 4500 Å were sequentially evaporated at a rate of 25 Å s^{-1} with pressure kept below 3×10^{-7} Torr during evaporation. Zr impurities were present in the Hf films at the level of ~5% as determined by backscattering analysis.

The second set of samples was prepared for sheet resistance and Hall coefficient measurements of Hf Si_2 formed on Si^e. Wafers covered with thermally grown SiO_2 were cleaned ultrasonically in TCE, acetone, and methanol. The wafers were then blown dry by nitrogen and loaded into the evaporation system. Si films 1300–2900 Å thick were evaporated, followed by deposition of Hf films of 500–1100 Å in thickness.

For Schottky barrier height (SBH) measurements of Hf Si_2, *n*-type ⟨111⟩ Si substrates of resistivity ~0.005 Ωcm covered with a 5 μm, 1.0 Ωcm *n*-type epilayer were used. Circular contact holes of ~1 mm diam were photolithographically defined on half of each of the wafers used. The other half was used for atomic depth profiling analysis. The same cleaning procedure that was used for the first set of samples was followed before loading the wafers for evaporation. Two sample configurations were prepared: (I) ⟨111⟩ Si/Hf; (II) ⟨111⟩ Si/Hf/Si^e/Hf.

All as-prepared samples were vacuum-annealed at temperatures between 575 to 715 °C at a background pressure of $\sim 5 \times 10^{-7}$ Torr. The silicide formation was monitored by 2 MeV $^4He^+$ backscattering spectrometry (BS). X-ray diffraction Read camera analysis was used to confirm the identity of the silicide phases formed. Forward and reverse I–V measurements were used to evaluate the SBH of the diodes. In cases where only a limited range of linearity was measured

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in the forward diode characteristics due to series resistance effect, the Norde method[9] or the improved Norde method[10] were applied to check the barrier height. The temperature during these measurements was ~22 °C. The Richardson constant A^{**} defined in Ref. 11 is assumed to be 112A K^{-1} cm^{-2}. A four-point probe of the Van der Pauw configuration was used to measure the sheet resistance and Hall coefficient at room temperature of the silicide layers of the second set of samples. In general, the samples used for such measurements were cleaved squares of ~1 cm × 1 cm. The magnetic field used was about 4 kG.

III. RESULTS AND DISCUSSIONS

A. Growth kinetics

Figure 1 shows 2 MeV $^4He^+$ BS spectra of a sample of ⟨100⟩ Si/2900 Å Hf/4500 Å Si^e after annealing at 600 °C for 120 min and at 650 °C for 15 min. The expected signal levels of Si and Hf for pure Si, Hf Si, and Hf Si_2 are also shown in the figure. The BS spectra show that a silicide with a Si to Hf atomic ratio ~2 forms between Si^e and Hf Si. X-ray diffraction confirms the presence of both Hf Si and Hf Si_2. No recrystallization of Si could be detected but the Read camera is not sensitive to that transformation. It can be deduced from BS that ~2000 Å of Si^e and ~600 Å of Si^c were consumed in the formation of Hf Si of ~4300 Å in thickness at all the annealing temperatures. The BS spectra of all the ⟨100⟩ Si/Hf/ Si^e samples annealed between 600 and 650 °C indicate that the Hf Si_2 that forms between Hf Si and Si^e is laterally quite uniform and has well-defined interfaces. These results are in marked contrast with the laterally nonuniform formation of Hf Si_2 that grows on Si^c only at temperatures in excess of 700 °C. This growth manifests itself by a uniform lowering of the Hf signal height in Hf Si, as reported by Ziegler *et al.*[3] Consistent with these facts, no detectable Hf Si_2 forms on the Si^c side of the Hf Si layer at temperatures lower than 650 °C, as is also quite evident from the BS spectra.

Figure 2 shows the square of thickness (X) of the Hf Si_2

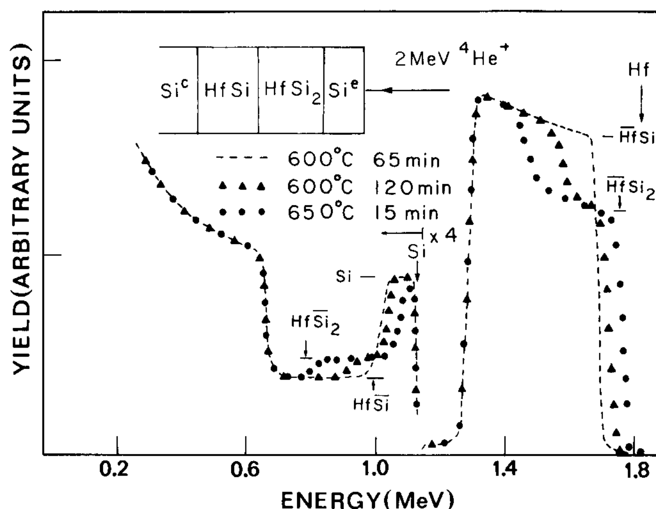

FIG. 1. 2 MeV $^4He^+$ BS spectra of samples with ⟨100⟩ Si^c substrate covered sequentially with about 2900 Å of Hf and about 4500 Å Si^e. Broken line: annealed at 600 °C for 65 min. Triangles: annealed at 600 °C for 120 min. Circles: annealed at 650 °C for 15 min.

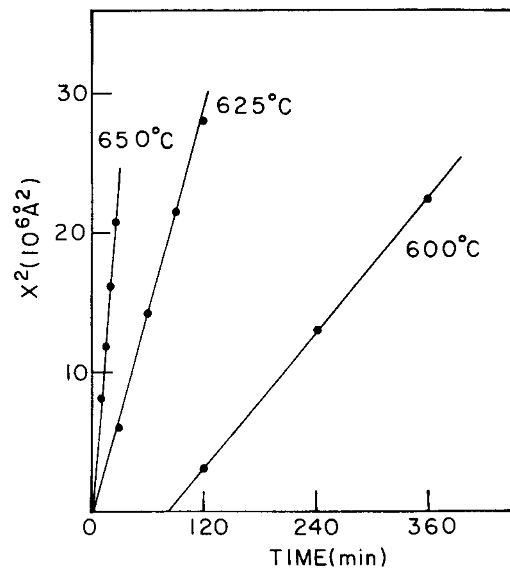

FIG. 2. Dependence of the thickness of Hf Si_2 on square root of annealing time at constant temperature. The lines are least square fit to the measured points.

layer that grows at the Hf Si/Si^e interface, plotted against annealing time for temperatures ranging from 600 to 650 °C. It can be seen that the data fit a parabolic growth law, which implies that the formation of Hf Si_2 from Si^e is a diffusion-controlled process, just like the formation of Hf Si from Si^c.[3] Figure 3 shows the Arrhenius plot of the growth rate shown in Fig. 2. The activation energy of the Hf Si_2 reaction for this narrow temperature range is estimated to be 3.5 ± 0.3 eV.

Previous studies to compare silicide formation from Si^c and Si^e have reported similar results. Interfacial contaminations have been suggested to account for the higher reaction temperatures in metal–Si^c systems than in the corresponding metal–Si^e systems, and lateral nonuniformities in silicide reactions between metal and Si^c as in the case of $TiSi_2$,[13] $CrSi_2$,[14] and $ErSi_2$.[16] Thermodynamic arguments involving formation energies considerations have been proposed to explain the low temperature formation of $NiSi_2$ and $CoSi_2$ on Si^e.[5,6,15]

In the present case of Hf Si_2, both interfacial contamina-

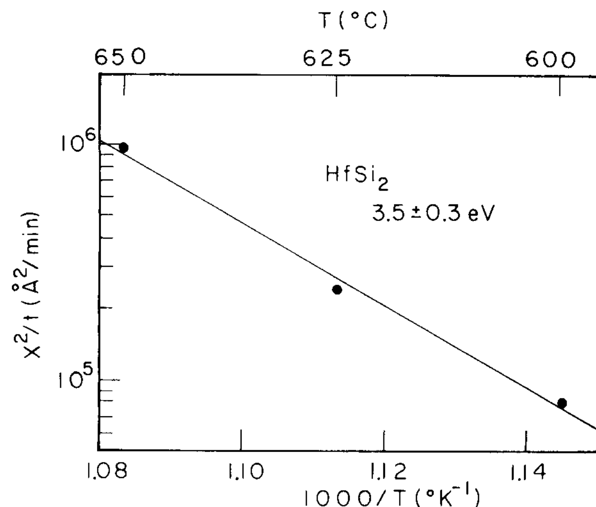

FIG. 3. Arrhenius plot of the growth rate as shown in Fig. 2. The activation energy for the growth of Hf Si_2 is 3.5 ± 0.3 eV.

tion and thermodynamic arguments may be invoked to explain why Hf Si_2 forms on Si^e at lower temperatures than on Si^c.

On a first thought it would seem that interfacial impurities may not inhibit the formation of Hf Si_2 from Si^c at ~600 °C since Hf Si_2 is not the first phase that forms between Hf and Si^c, and that the formation of Hf Si, the first phase at ~550 °C indicates that the effect of impurities on atomic transport could be overcome at temperatures above 550 °C. However, careful considerations of the evolution of interfacial impurities like oxygen as from recent studies[17] suggests that some interfacial impurities present between Hf and Si^c would tend to accumulate at the Hf Si/ Si^c interface after solid–phase reaction, since Si is the dominant moving species during the formation of Hf Si.[18] It is not impossible that impurities residing at the Hf Si/Si^c interface might subsequently suppress the formation or nucleation of Hf Si_2 at temperatures below 700 °C. We believe that the interface between Hf and Si^e evaporated sequentially without breaking vacuum is cleaner than that between Hf and Si^c; hence, the effect of interfacial impurities is reduced in the formation of Hf Si_2 from Si^e.

On the other hand, thermodynamic arguments may also be suited to explain the low temperature formation of Hf Si_2 on Si^e as in the case of $NiSi_2$ or $CoSi_2$.[5,6] The arguments are based on the idea that Si^e has a positive formation energy because it is not crystalline. Previous studies show that Si^e in contact with a silicide layer crystallizes upon thermal annealing between about 190 and 730 °C,[19] depending on the conditions prevailing. To apply the thermodynamic argument, we assume that in the present experiment, Si^e remains amorphous. Since Si^e has a positive formation energy, the driving force for silicide formation is increased over that of Si^c. But if the silicide is unstable (or barely stable) at low temperature, the positive formation energy of Si^e will decrease the silicide formation temperature. There are two possibilities of having an unstable Hf Si_2. In one case, the bulk phase may not exist in thermal equilibrium at low temperatures, as is the case for PdSi,[20] and as was suggested for $NiSi_2$. In the other case, the negative reaction enthalpy of the formation of Hf Si_2 from Si^c may be so small that the contribution from interface and strain energies make thin Hf Si_2 film formation from Si^c unfavorable below a threshold temperature. (The value for the reaction enthalpy of Hf Si_2 reaction from Hf Si and Si^c is not available.) In both cases, when the temperature exceeds a certain critical value (which is referred to as "pseudocritical" temperature by Baglin *et al.*[4]), silicide will form. But if the diffusion rates are large above this critical temperature, the growth of silicide is controlled by heterogeneous nucleation, and hence layer-by-layer formation is not observed. In fact, if we extrapolate the formation rate of Hf Si_2 from Si^e to 700 °C, a 2900 Å Hf film will be fully consumed to form Hf Si_2 in less than a minute. Because of the elevated free energy of Si^e, Hf Si_2 will exist with Si^e but not with Si^c at low temperatures.

B. Four-point probe characterization

As an additional piece of evidence to show that Hf Si_2 grows in a layer-by-layer fashion from Si^e, sheet conductance σ_s and sheet Hall coefficient R measurements were made on the $SiO_2/Si^e/Hf$ samples annealed at different times and temperatures ranging from 575 to 650 °C. The sample configuration was established by BS to be of the general form $SiO_2/Si^e/Hf\,Si_2/Hf\,Si$.

For two uniform layers of silicide connected in parallel electrically, σ_s/to is a linear function of $R\sigma_s^2/to$, where to is the thickness of the as-deposited metal film. Figure 4 shows the relationship between σ_s/to and $R\sigma_s^2/to$.[8] Filled and open circles are experimental points from samples with Hf thickness (to) of ~1100 and 500 Å, respectively. The data fits a linear relationship reasonably well. This shows that the Hf Si/Hf Si_2 bilayer can be modeled electrically as two conducting layers connected in parallel. Both silicides exhibit n-type conductivities. From the measurement on the samples in which Hf Si was completely consumed to form Hf Si_2, the electron concentration and Hall mobility in Hf Si_2 were determined to be $2.9 \pm 0.2 \times 10^{21}$ cm^{-3} and 36 ± 4 cm^2/Vs, respectively. The resistivity of Hf Si_2 is determined to be 60 ± 3 $\mu\Omega$ cm, a value that is very close to that reported by other authors.[2,12]

C. Schottky barrier height measurements

Two samples of the following configurations were prepared: (I) ⟨111⟩ Si/Hf (~440 Å); (II) ⟨111⟩ Si/Hf (~70 Å)/Si^e (~550 Å)/Hf (~370 Å). From BS spectra, Hf Si forms in sample (I) after annealing at temperatures between 575 and 675 °C. Annealing above 700 °C results in the formation of Hf Si_2 from Hf Si. The configuration of sample (II) is designed such that the bottom 70 Å of Hf react with Si^e to form Hf Si_2, and the top Hf layer consumes the Si^e to form adjacent layers of Hf Si_2 and Hf Si for annealing temperatures between 600 and 700 °C. Not all the Hf Si transforms into Hf Si_2 below 700 °C because of the limited amount of Si^e available. The final sample configuration after annealing above 700 °C is the same as that of sample (I) taken through the same heat treatment. BS analysis confirms the formation

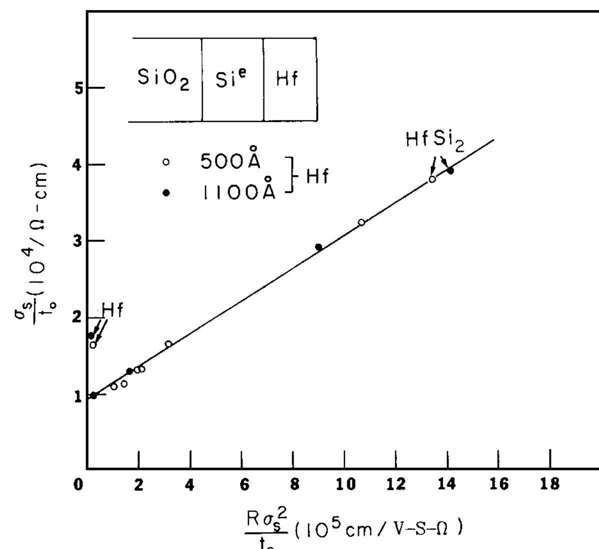

FIG. 4. σ_s/to vs $R\sigma_s^2/to$ data points for samples containing to silicide phases. Data points of samples with only Hf or Hf Si_2 on Si^e are indicated.

TABLE I. The table lists Schottky barrier heights (in eV) of Hf silicides on a n-type ⟨111⟩ Si in samples (I) (Si^c/Hf) and (II) (Si^c/Hf/Si^e/Hf). The barrier height was measured with forward I–V (the ideality factor is indicated in the parentheses) and reverse I–V characteristics. The uncertainty for all the barrier height values is about 0.01 eV.

Sample type	Temp (°C) / Time (min)	575 / 30	600 / 30	625 / 30	650 / 30	675 / 30	715 / 30
I	Silicide	Hf Si	Hf Si	Hf Si	Hf Si	Hf Si	Hf Si_2
	Forward I–V	0.50 (1.08)	0.50 (1.10)	0.50 (1.06)	0.50 (1.09)	0.49 (1.09)	0.54 (1.04)
	Reverse I–V	0.50	0.49	0.50	0.49	0.49	0.53
II	Silicide			Hf Si_2	Hf Si_2	Hf Si_2	Hf Si_2
	Forward I–V			0.53 (1.06)	0.53 (1.07)	0.53 (1.07)	0.54 (1.05)
	Reverse I–V			0.54	0.53	0.53	0.54

of the ⟨111⟩ Si/Hf Si_2/Hf Si configuration in sample (II) after annealing at temperatures below 700 °C and the presence of a single layer of Hf Si_2 in contact with ⟨111⟩ Si for annealing temperatures higher than 700 °C. Table I summarizes the silicides formed in contact with the Si substrate in samples (I) and (II) and the SBH of the silicides. The results of sample (I) show that the SBH of Hf Si is 0.50 ± 0.01 eV and is stable up to 700 °C. Upon the formation of Hf Si_2 at 715 °C, the SBH increases to 0.54 ± 0.01 eV. For sample (II), the SBH of Hf Si_2 formed from Si^e above 600 °C is essentially the same as that of Hf Si_2 in sample (I) within experimental uncertainties.

The observation is quite different from that of $CoSi_2$ [7] and $ErSi_2$ [16] studied recently. In the $CoSi_2$ case, the SBH of $CoSi_2$ formed by reacting Co with Si^e in a configuration same as that in sample (II) is about 0.2 eV higher than that of $CoSi_2$ formed between Co and Si^c. The discrepancy in the SBH values is attributed to the difference in the lateral uniformity of $CoSi_2$/Si^c interface on different samples as determined by BS analysis. In the case of $ErSi_2$, difference in SBH on p-type Si is observed because of the formation of deeply penetrating surface pit when Er reacts with Si^c. The presence of such pits affects the electronic properties of $ErSi_2$/Si^c interface drastically. In our Hf Si_2/Si^c system the atomic depth profile of samples (I) and (II) after annealing at 715 °C are determined carefully by BS analysis, which, in fact, revealed comparable lateral uniformity of the Hf Si_2/Si^c interfaces. On the other hand, evaluation of surface morphology by optical microscopy indicates that surface pits are absent in both samples (I) and (II) after heat treatment at 715 °C, although the surface of sample (I) is observed to be rougher than that of sample (II), which is probably due to different grain size or structure in the sample. Hence, it appears that in the case of Hf Si_2 the SBH of Hf Si_2 on Si^c is not so sensitive to the method of preparation as in $CoSi_2$ or $ErSi_2$. There is, however, one common characteristic shared by all three cases: the disilicide can be formed in contact with Si^c at lower temperatures if Si^e is used to react with the metal in a configuration similar to that of sample (II) than if the metal reacts directly with Si^c.

It is worth noting that the SBH values of 0.50 eV for Hf Si and 0.54 eV for Hf Si_2 on n-type Si measured in our present investigations are quite different from the values reported previously by other authors,[1,2] who measured SBH of ~0.53–0.56 eV for Hf Si and ~0.60 eV for Hf Si_2 on n-type Si. The reason for this difference is not clear. It can be due to different crystal orientations of Si used or different methods of surface preparation of Si^c before Hf evaporation.

IV. SUMMARY

We have shown that Hf Si_2 can be formed by a reaction between Hf Si and evaporated Si at temperatures between 575 and 650 °C. The growth of Hf Si_2 occurs in a layer-by-layer manner. The thickness of Hf Si_2 is proportional to the square root of time at a fixed temperature. The activation energy of this reaction is about 3.5 eV. The Hf Si and Hf Si_2 layers formed from Si^e and Hf can be modeled electrically as two uniform conducting layer connected in parallel. These results are in marked contrast with the formation of Hf Si_2 on single crystal Si. ⟨111⟩ Si/Hf Si_2 diodes can be formed at temperatures above 600 °C by reacting Hf with evaporated Si in a ⟨111⟩ Si/Hf/Si^e/Hf configuration. The SBH of Hf Si_2 on n-type ⟨111⟩ Si formed in this manner is determined to be about 0.54 eV, which is the same as that when Hf reacts directly with Si^c to form Hf Si_2 above 700 °C.

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