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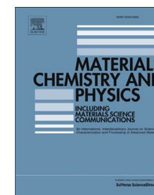

Growth of hafnium and zirconium silicides by reactive diffusion

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HIGHLIGHTS

- Growth mechanisms of hafnium and Zr silicides by reactive diffusion are explained.
- Only two phases are grown in the interdiffusion zone.
- Diffusion parameters are estimated.
- Location of the Kirkendall marker plane indicates that Si is the faster diffusing species in disilicides.
- This indicates that vacancies are present on the Si sublattice in disilicides.

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ABSTRACT

Diffusion controlled growth of the phases in Hf–Si and Zr–Si systems are studied by bulk diffusion couple technique. Only two phases grow in the interdiffusion zone, although several phases are present in both the systems. The location of the Kirkendall marker plane, detected based on the grain morphology, indicates that disilicides grow by the diffusion of Si. Diffusion of the metal species in these phases is negligible. This indicates that vacancies are present mainly on the Si sublattice. The activation energies for integrated diffusion coefficients in the $HfSi_2$ and $ZrSi_2$ are estimated as 394 ± 37 and 346 ± 34 kJ mol^{-1}, respectively. The same is calculated for the HfSi phase as 485 ± 42 kJ mol^{-1}. The activation energies for Si tracer diffusion in the $HfSi_2$ and $ZrSi_2$ phases are estimated as 430 ± 36 and 348 ± 34 kJ mol^{-1}, respectively.

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1. Introduction

Transition metal silicides draw special attention because of their use in microelectronic devices as Ohmic contacts and Schottky barriers [1]. Low resistivity, metal like behavior and high temperature stability make them attractive from application point of view [2–5]. Hf and Zr silicates are being considered for replacing silica in sub 100 nm complementary metal oxide semiconductor (CMOS) technology [6]. Advantages of introduction of Hf and Zr films at the Si/SiO_2 interface are being examined [5,7].

To date, several studies have been conducted to examine the growth of the phases in Hf/Si in thin film couples [8–11]. There are five phases in this system [12], however, only two phases, $HfSi_2$ and HfSi are found to grow in the interdiffusion zone. Unlike bulk diffusion couple, sequential growth of phases is very common in thin film couples [13,14]. In this system, HfSi is found to grow first, followed by $HfSi_2$ which grows very rapidly at the $Si/HfSi_2$ interface by nucleating on HfSi [11,15]. Parabolic growth has been found, which indicates diffusion controlled growth of the phases [15]. Ziegler et al. [11] studied the growth of the HfSi and $HfSi_2$ phases in the temperature range of 550–750 °C and 750–900 °C respectively, in the He atmosphere, and estimated the activation energy for growth to be 2.5 eV (241 kJ mol^{-1}). Movement of the impurities during the growth of this phase indicated that Si is the faster diffusing species. So et al. [15] studied the growth of the $HfSi_2$ phase in the temperature range of 600–650 °C in vacuum and calculated the activation energy as 3.5 ± 0.3 eV (337 ± 29 kJ mol^{-1}). No diffusion studies have been conducted in bulk condition to date, hence no reliable information is available understanding the growth mechanism of phases compared to the study in thin film condition.

Unlike the Hf–Si system, studies on diffusion controlled growth of the phases in the Zr/Si system are very limited [16,17]. In one of the studies [16], growth of the phases in bulk diffusion couples was reported, however, analysis on diffusion process was not done. Although there are six phases present in the system [18], only two phases, $ZrSi_2$ and ZrSi are found to grow. After the consumption of Si, other phases were found between $ZrSi_2$ and Zr.

Therefore, the aim of this present study is to conduct bulk diffusion couple experiments in these two systems to analyze the

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growth mechanism of the phases and the diffusion mechanism of the species. Time dependent experiments are conducted to examine the diffusion controlled growth of the phases, and temperature dependent experiments to calculate the activation energies. Grain morphology in the interdiffusion zone indicates relative mobilities of the species, which help to predict defects and diffusion of elements.

2. Experimental procedure

1 mm thick refractory metals of Hf and Zr with 99.95 wt % purity, 0.7 mm thick (100) oriented one side polished Si wafer with 99.999 wt% purity were used in this study. Hf and Zr pieces were ground and polished following standard method and cleaned ultrasonically in acetone. Bonded halves were clamped in a special fixture and annealed in a calibrated vacuum tube furnace ($\sim 10^{-4}$ Pa). Hf/Si couples were annealed in the temperature range of 1150–1250 °C and Zr/Si couples were annealed in the temperature range of 1100–1250 °C for 16 h. Temperatures were controlled within ±5 °C. Time dependent experiments to examine the diffusion controlled growth of the phases were conducted for 4–36 h at 1250 °C. Temperature range was selected such that we get reasonable difference in the thickness of phase layers for minimum error in quantitative analysis. Subsequently, samples were mounted in resin and cross-sectioned by a slow speed diamond saw. Final polishing was done with 0.04 μm colloidal silica. Interdiffusion zones were examined in a scanning electron microscope (SEM) and the compositions profiles were measured by an electron probe microanalyzer (EPMA). Samples were etched by an acid mixture of 45 vol.% HNO_3 and 55 vol.% HF to reveal grain morphology.

3. Results and discussion

Backscattered electron images (BSE) of interdiffusion zones of Hf/Si and Zr/Si diffusion couples annealed at 1200 and 1250 °C for 16 h, respectively, are shown in Fig. 1a and b. X-ray diffractions taken in these diffusion couples are shown in Fig. 1c and d. Only disilicide and monosilicide phases grew in the interdiffusion zone, although there are many phases present in both the systems. Moreover, the thickness of the disilicides is much higher than the monosilicide, which indicates difference in the growth rates.

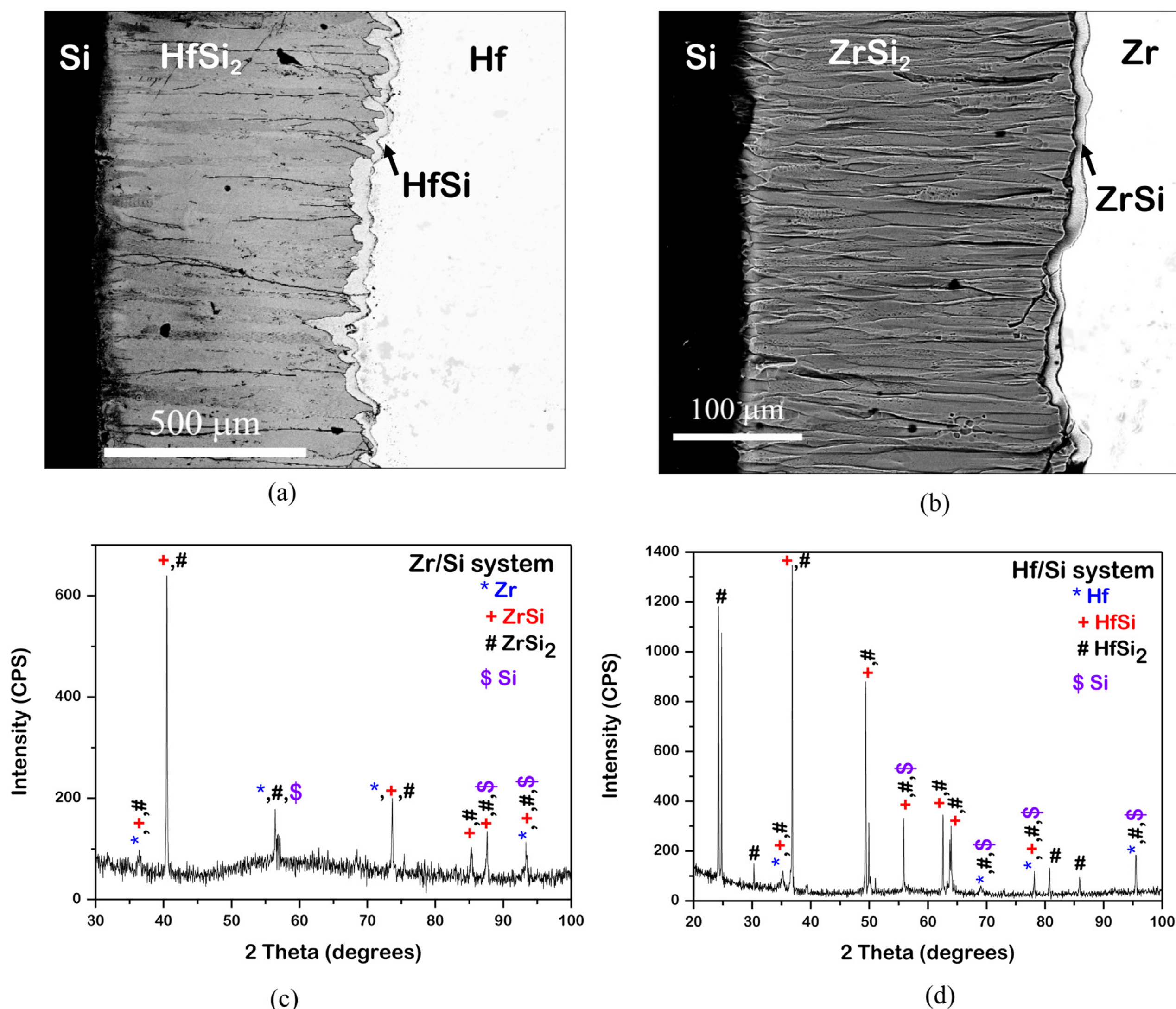

Fig. 1. Scanning electron micrograph of etched (a) Hf/Si diffusion couple annealed at 1250 °C for 16 h (b) Zr/Si diffusion couple annealed at 1200 °C for 16 h, (c) and (d) are the X-ray analysis confirming the phases detected in the interdiffusion zone.

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