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Hafnium silicide formation on Si(001)

H. T. Johnson-Steigelman, A. V. Brinck, S. S. Parihar, and P. F. Lyman*
Laboratory for Surface Studies and Physics Department, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211, USA
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The solid-state reaction of thick (~50 nm) and thin (~monolayer) films of Hf with cleaned and oxidized Si(001) substrates was investigated. Upon annealing to 1000 °C, films of $HfSi_2$ were formed after reaction times that depended upon the surface condition of the substrate before deposition. The chemical state of the reacted surfaces was characterized using x-ray photoelectron spectroscopy, and the shifts in binding energy upon silicide formation were recorded. Even for thick films, low-energy electron diffraction (LEED) revealed that the (2×1) pattern of the Si substrate emerged, suggesting that three-dimensional islanding of the $HfSi_2$ film had occurred. The islanding behavior was investigated for both thick and thin films using LEED, atomic force microscopy, and scanning electron microscopy. Streaking in the LEED patterns for the thick films suggest that the island morphology is influenced by the underlying Si substrate.

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INTRODUCTION

The continued miniaturization of circuit elements in ultralarge-scale integrated (ULSI) circuits has required that the SiO_2 layer that forms the gate oxide of field-effect transistors be made thinner and thinner. Eventually, a fundamental limit on the thickness of an effective insulating SiO_2 barrier will be reached when the layer is so thin that electron tunneling provides a current leakage path that is unacceptably high for low-power devices. This limit is expected to be reached within a few years. As a result, an intensive search has been launched for a material having a higher dielectric constant than SiO_2 that could serve as the gate oxide. Such a "high-κ" insulator would allow the gate oxide to be physically thicker (for a given capacitance), dramatically reducing tunneling. However, to serve as an effective gate insulator, any replacement for SiO_2 must possess the many favorable electrical and structural properties of the SiO_2/Si interface. In particular, it is thought that oxides and silicates of Hf and Zr may exhibit an interface with Si that is stable against deleterious SiO_2 formation, but would possess many of the desirable interface attributes of SiO_2.[1,2]

Hf forms stable silicates $HfSi_xO_y$ with a range of Hf/Si ratios.[2] To provide the smallest deviation from the mature techniques established for device construction, it makes sense to produce hafnium silicate films with a small Hf/Si ratio if they can meet the electrical and physical requirements of a gate insulator. It has been asserted that a relatively small amount of Hf can significantly increase the dielectric constant of SiO_2,[3,4] although, for the related case of Zr, this finding has been called into question.[5,6] Structurally, it has been found that hafnium silicates with a small Hf/Si ratio readily form stable amorphous compounds,[7] which are desirable in a gate oxide to reduce electrical leakage and dopant diffusion along grain boundaries. The present paper reports our investigation of the formation of hafnium silicide films, which could then be oxidized to form a hafnium silicate.[8] To minimize the Hf/Si ratio, and in light of the fact that any $HfSi_x$ phase in the vicinity of the Si substrate will form the disilicide upon annealing, we have concentrated on the formation of the most Si-rich stable silicide phase, $HfSi_2$.

The Hf/Si system has been investigated previously in the hope of forming silicide device interconnects having low sheet resistance and contact resistivity.[8–10]. In these works, Hf was deposited on Si substrates, and the kinetics of the reaction to form HfSi and then $HfSi_2$ were monitored. Notable findings were that HfSi and $HfSi_2$ formed readily at temperatures as low as 600 and 765 °C, respectively. Si was found to be the dominant diffusing species. For a film of Hf on crystalline Si, HfSi would form in a layerwise fashion between the Si substrate and the unreacted Hf, but the formation of $HfSi_2$ would nucleate heterogeneously[9] unless excess Si was supplied in the form of an amorphous Si capping layer.[10] Later work focused on the thin (~12 nm) amorphous hafnium silicide layer that is formed at the Hf/Si interface at annealing temperatures of 400–500 °C.[11–13]

In the present work, we report results on the formation of $HfSi_2$ by the solid-state reaction of metallic Hf with Si(001) substrates. We also investigated the effect on this reaction of a layer of SiO_2 at the interface between the deposited Hf film and the substrate. The chemical state and compound formation was probed using x-ray photoelectron spectroscopy (XPS) and powder x-ray diffraction (XRD), while important inferences about the morphology of the reacted film were derived from low-energy electron diffraction (LEED), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Because our primary interest is on the eventual production of hafnium silicate films with a small Hf/Si ratio, this study emphasized the formation of $HfSi_2$ over the more Hf-rich phases formed at lower temperatures.

EXPERIMENT

Hafnium silicide formation was studied in two regimes: thick films (~50 nm) and thin films (~monolayer, ML). For all experiments, the substrates consisted of commercial Si(001) wafers (p type, 5 Ω cm). Hf films were deposited in either high vacuum (HV) (for the thick films) or ultrahigh vacuum (UHV) (for the thin films), and were subsequently annealed to various temperatures to initiate the silicidation reaction. Because our primary interest is on the eventual pro-

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duction of hafnium silicate films with a small Hf/Si ratio, this study emphasized the formation of $HfSi_2$ over the more Hf-rich phases formed at lower temperatures.

Samples were analyzed by XPS and low-energy electron diffraction (LEED) in a VG Mk. II ESCALab UHV chamber with a base pressure of less than 1×10^{-10} torr. Unmonochromated Al $K\alpha$ radiation was used to excite the photoelectrons, and spectra were acquired with near-normal electron emission. In addition to a survey spectrum, detailed scans (instrumental resolution $\leqslant$0.95 eV) of the O 1s, C 1s, Si 2p, and Hf 4f regions were acquired for each surface condition. Binding energies were referenced to the Ag $3d_{5/2}$ core level, assumed to lie at 368.27 eV, and were determined with an estimated overall precision of ±0.05 eV.

After XPS and LEED analysis, some samples were transported in air to an ABT-32 scanning SEM, where images were acquired and energy-dispersive x-ray spectroscopy (EDX) scans were performed. Other samples were scanned using an atmospheric AFM. SEM, EDX, and AFM measurements took place within days of sample production. Although the surface is expected to have oxidized during transit, morphological features should remain on the surface.

Thick films

For the thick-film studies, Si(001) wafers with three different surface oxidation conditions were prepared prior to Hf deposition. One set of samples was placed in a box furnace at 900 °C for 6 h to form a thermal oxide, calculated to be ~50 nm using the Deal-Grove model.[14] Another set of samples was used as-received, with a ~1.5-nm native oxide. The third set of samples was stripped of its native oxide using dilute HF acid immediately before insertion into a HV electron-beam evaporator. Hf was deposited at $\sim10^{-5}$ torr on the three types of substrate samples, which were held at room temperature (RT). Stylus profilometry indicated that the deposited Hf layers were 50 to 80 nm thick. These samples were then transferred through air to the UHV chamber for annealing and analysis. During prolonged annealing of samples to 1000 °C, the pressure of the UHV chamber rose from its base pressure to $\sim2\times10^{-9}$ torr.

Thin films

For the thin-film studies, Si(001) samples were inserted into the UHV chamber as received, were degassed, and then resistively heated to 1000 °C, rendering a clean (2×1)-reconstructed surface. Submonolayer to ML amounts of 99.9% pure Hf (excluding ~3% Zr) were deposited on the substrates using an electrostatic electron beam evaporator.[15] The samples were held at RT, and the pressure typically rose to $\sim5\times10^{-9}$ torr during deposition. As a control, one sample was prepared identically, including operation of the Hf evaporator, but was not exposed to Hf vapor. XPS and LEED measurements were carried out immediately after deposition and then again after subsequent anneals.

RESULTS

Thick films

Before annealing, no Si features appeared in the XPS spectrum. The only Hf feature evident stemmed from HfO_2 (from the native oxidation of the deposited Hf films).[16] Although it had been reported long ago[9] that Hf and Si react at temperatures as low as 600 °C to form HfSi and at 765 °C to form $HfSi_2$, little change in any of our samples, either visually or by XPS, was observed upon annealing to temperatures less than 950 °C. (However, XPS is only sensitive to the outermost several nm.) The only change observed at these temperatures was a reduction of the HfO_2 thickness in some samples evidenced by the introduction a metallic feature in the Hf 4f spectra. No spots appeared in the LEED pattern from these samples, indicating that the deposited surface layer lacked long-range order.

Upon annealing to 1000 °C, however, the visual appearance of all samples changed dramatically, from dark metallic silver to a matte gray. Importantly, however, the amount of time that must elapse at this annealing temperature before this visual change occurs varied greatly with substrate surface oxidation condition. Specifically, the HF-etched samples reacted in ~10 mins, the samples having a native oxide took ~1–2 hs, and the thermally oxidized samples took from 3 to 12 hs at 1000 °C. Thus, SiO_2 appears to form a barrier that slows the interdiffusion necessary for this reaction to proceed.

For all of the samples, the condition after heating to 1000 °C was similar. After annealing (with the concomitant change in visual appearance), all samples gave rise to essentially the same XP spectra; specifically, the Hf 4f region contained only one sharp spin-orbit doublet, and Si was apparent, as shown in Fig 1. The Hf 4f doublet was extremely narrow, with a linewidth of $\leqslant$0.95 eV, and the binding energy (BE) of the $4f_{7/2}$ feature was 14.65 eV. For comparison, we determined the BE of metallic Hf to be 14.35 eV, in good agreement with published reports of 14.31 eV (Ref. 16) and 14.3 eV (Ref. 17). Metallic Hf shows a pronounced asymmetry in the XPS line shape;[16] upon conversion to $HfSi_2$, the asymmetry of the Hf 4f line shape was greatly reduced. (The Doniach-Sunjic asymmetry parameter[18] decreased from 0.32 to 0.14 upon silicidation.) The Si $2p_{3/2}$ line exhibited a prominent feature at 99.45 to 99.50 eV [see Fig. 1(b)]. This peak is essentially indistinguishable from that of substrate Si, which we determined to have a Si $2p_{3/2}$ BE of 99.5 eV.[19] Notable by its absence in XPS, even for samples initially containing a 50-nm SiO_2 layer, was any feature in the O 1s region.

Structural order in the film was probed with LEED and x-ray diffraction (XRD). Remarkably, samples annealed at 1000 °C for several hours gave rise to a (2×1) LEED pattern reminiscent of the clean surface of Si(001) (see Fig. 2). Subsequent powder XRD confirmed that annealed samples were completely or dominantly composed of $HfSi_2$. Thus, on the basis of diffraction techniques, we conclude that the film is composed of crystalline or polycrystalline $HfSi_2$, and that the surface of the specimen displays long-range order.

It is possible to explain these findings by the formation of an epitaxial $HfSi_2$ layer; this layer could have a (2×1) reconstruction explaining its resemblance to the clean Si(001) pattern. However, these findings are also consistent with the formation of a $HfSi_2$ film that has undergone three-dimensional islanding. The formation of islands will expose portions of the substrate to the vacuum, allowing the emer-

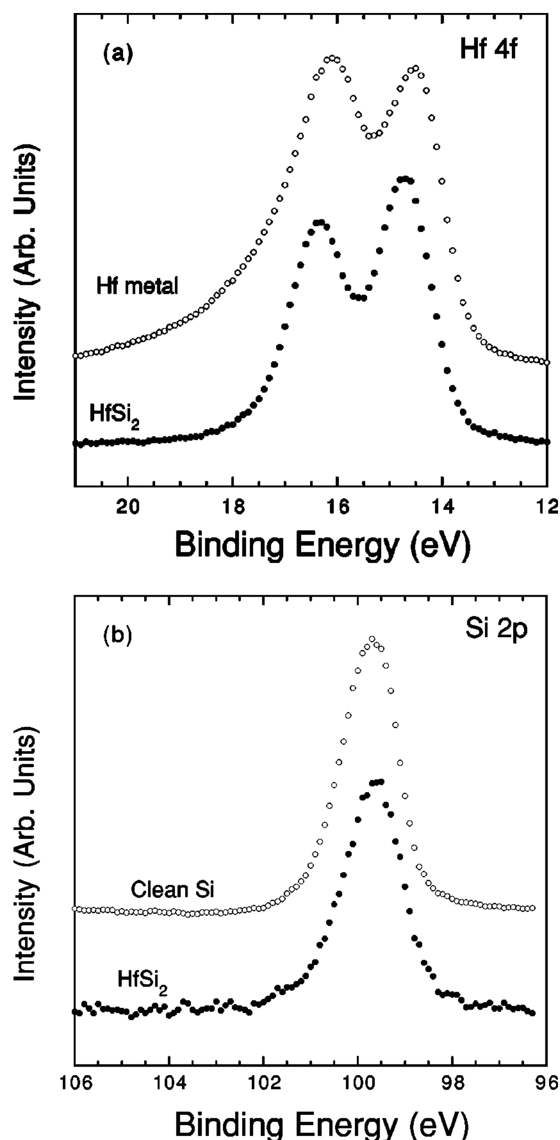


FIG. 1. XP spectra from $HfSi_2$ sample formed on HF-etched Si(001) and annealed to 1000 °C for 50 min. Reference spectra from bulk Hf and Si are shown for comparison. Spectra are scaled to the same height and are offset for clarity. (a) Hf 4f XPS spectrum from thick (~50 nm) $HfSi_2$ sample (bottom) and clean metal Hf foil (top). (b) Si 2p spectrum from thick $HfSi_2$ sample (bottom) and clean Si(001)-(2×1) (top).

gence of a LEED pattern from the substrate. Other evidence, discussed below, strongly favors this latter interpretation.

For many of the samples that underwent prolonged annealing and resultant islanding, a Si $2p_{3/2}$ feature at 101.2 eV BE and a C 1s feature near 284.1 eV BE, both attributable to SiC, became evident in XP spectra, as shown in Fig. 3. The island interpretation of the LEED pattern is supported by SEM imaging of the annealed samples. (No preanneal imaging was conducted.) Figure 4 reveals typical surface morphology of one of the thick-film samples. The features consist of roughly circular islands with average diameters ~400 nm to ~500 nm, but in many cases, two or more of these islands merge into longer features. EDX spectra (not shown) reveal a noticeably higher concentration of Hf in the

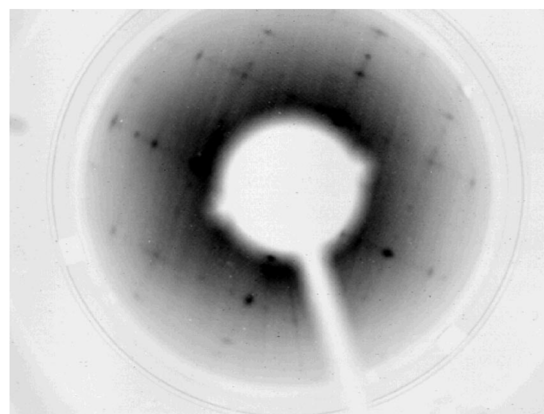


FIG. 2. LEED pattern acquired at 70 eV from thick (~50 nm) $HfSi_2$ film on HF-etched Si(001) after annealing at 1000 °C for 3 h. For clarity, the video image has been inverted.

bright features as compared to the darker areas between them.

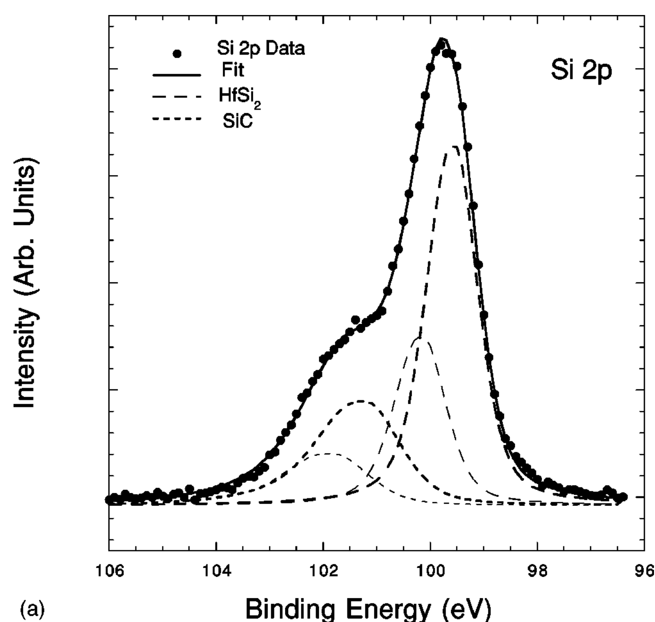
Figure 5 depicts a typical AFM image of a thick-film sample after annealing. The mottled surface suggests the formation of islands. Typical sizes of these features are 150 nm×220 nm. The average feature height above the lowest point in the image is 52 nm±8 nm. The areas between the features are presumably exposed substrate.

Thin films

Upon RT deposition of ~1 ML Hf onto a clean Si(001) -(2×1) surface, no spots were visible in the LEED pattern, indicating a complete destruction of the surface's long-range order by the reactive metal film. The Hf 4f XP spectrum (Fig. 6) showed a single broad feature centered near 16.0 eV BE (which includes contributions from the $4f_{7/2}$ and $4f_{5/2}$ lines). The feature lacked the asymmetric tail characteristic of metallic Hf. It is not possible to uniquely decompose this peak, but it can be accounted for either as one Hf 4f silicide doublet with twice the usual width, or as a combination of several doublets each having the silicide line shape and slightly displaced BE. The result is consistent with an inhomogeneous layer of Hf atoms bound to Si, but not fully reacted. The Si 2p spectra did not reveal any surface components attributable to Hf bonding. However, as demonstrated with the thick films, little BE shift is expected upon reaction with Hf, and moreover the data were not acquired in a surface-sensitive mode.

Upon annealing to 750 °C for 5 min, the Hf 4f spectral features coalesced into a sharp doublet characteristic of the silicide phase, as shown in Fig. 6. The BE of the $4f_{7/2}$ peak was 14.6 eV, which is about 0.6 eV shallower than prior to annealing. Moreover, the LEED pattern changed back to a (2×1) reminiscent of the clean surface (albeit with higher background and broadened features).

This process was repeated several times, with additional Hf metal being deposited at RT, which removed the LEED pattern and broadened the XPS features; upon reannealing, the (2×1) pattern reemerged each time and the XPS features



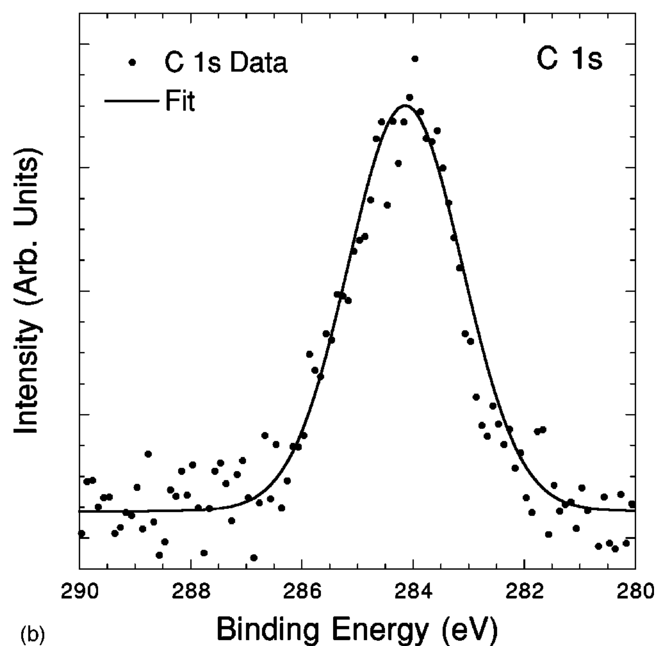


FIG. 3. XP spectra acquired from thick (~50 nm) $HfSi_2$ sample. Hf was deposited on thermally oxidized Si(001) after annealing at 1000 °C for 12 h. Fits are shown by solid lines. A Shirley background was subtracted before fitting. (a) Si $2p$ spectrum. The long (short) dashed lines correspond to the $HfSi_2$ (SiC) components. (b) C $1s$ spectrum from same sample. The peak position is consistent with SiC formation.

sharpened into a silicidelike line shape with a $4f_{7/2}$ component at 14.6–14.7 eV BE. These observations suggest that the Hf, upon annealing to 750 °C, gathered into $HfSi_2$ islands on the surface, exposing the substrate beneath.

An AFM image of a sample prepared with Hf as above is shown in Fig. 7. Features can be classified into two size categories, large and small. Large features had typical lateral dimensions of 110 nm × 150 nm, with typical heights of ≈10 nm. Small features had typical lateral dimensions of

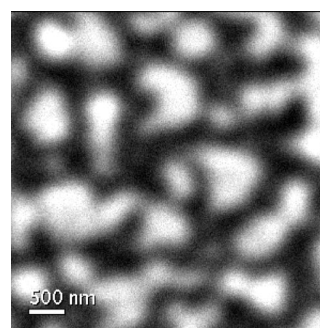


FIG. 4. SEM image from thick (~50 nm) $HfSi_2$ sample on thermally oxidized Si(001) after annealing at 1000 °C for several hours.

50 nm × 70 nm, with typical heights of 1–2 nm. A control sample, which was subjected to the same processing conditions with the exception that no hafnium was deposited, exhibited only the large features.

Comparison of these samples suggests that the small features in Fig. 7 are related to the formation of Hf or $HfSi_2$ islands, while the large features may be attributed to some extraneous contamination inherent to the sample preparation. Possibilities include contamination occurring before sample loading, or SiC cluster formation[20] either during sample cleaning or due to the elevated pressure during operation of the Hf evaporator. Hafnium-covered samples that were not annealed (not shown) were similar to those that were annealed without hafnium, i.e., they lacked the small features seen on the hafnium-covered and annealed samples. SEM of the thin-film samples did not reveal any visible features to the limit of the instrument. This observation is consistent with the feature sizes found in AFM. The concentration of Hf was below the detection limits for EDX analysis.

DISCUSSION

Evidently, Hf and the Si substrate are able to react at 1000 °C despite the presence of a SiO_2 layer at the interface with a thickness of up to 50 nm, and no O is observed after this annealing treatment. Recent studies suggest that Hf metal[1] or even substoichiometric HfO_x films[21] are able to reduce SiO_2 layers. In the present study, the O that was originally at the interface may have diffused into the bulk, or it

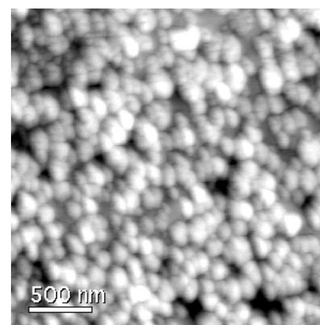


FIG. 5. AFM image (contact mode) from thick (~50 nm) $HfSi_2$ sample on Si(001). The sample was annealed for 5 h at 1020 °C.

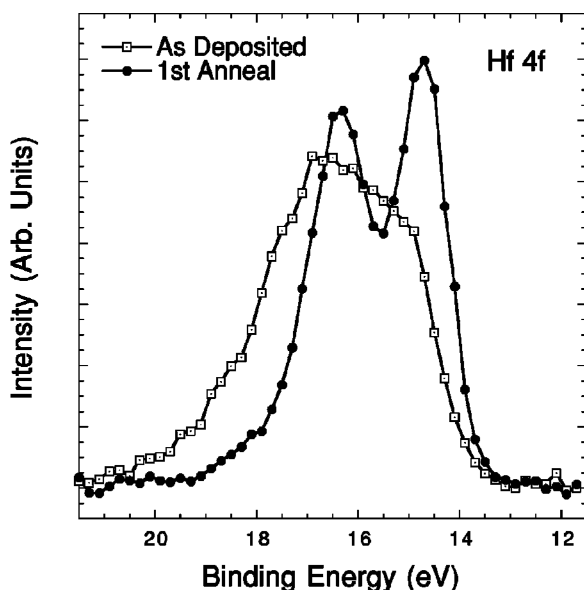


FIG. 6. Hf 4*f* XP spectra acquired from thin (~ML) Hf deposited at RT on clean Si(001)-(2×1) before and after annealing to 750 °C for 5 min. The lines are a guide to the eye.

may have diffused to the surface and desorbed. Although we cannot distinguish these outcomes, it seems more likely that O was desorbed, probably as SiO as known for the thermal breakdown of SiO_2 films. This supposition can explain why the time required to completely react the surface increased with the thickness of the substrate oxide layer. (Of course, it is also possible that a silicate layer containing O remains at the interface; however, in other studies conducted in our laboratory,[1,22] hafnium silicate layers were observed to break down to $HfSi_2$ under vacuum annealing to 1000 °C.)

After formation of the silicide phase, there are a number of observations that imply that three-dimensional clusters or islands occur on the surface of both the thin and the thick samples. While it is possible that an epitaxial $HfSi_2$ layer formed, the simplest explanation supported by the experimental evidence is island formation. For thick films annealed for several hours in UHV, a LEED pattern characteristic of the clean surface appears. The appearance of this pattern from a ~50–80-nm film is difficult to explain except if the $HfSi_2$ film forms three-dimensional structures, thus allowing a fraction of the bare surface to be exposed. A few samples

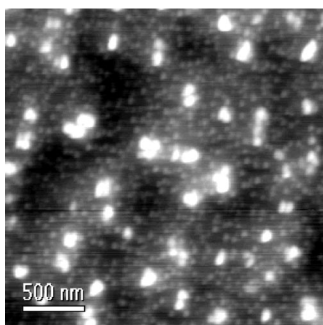


FIG. 7. AFM image from thin (~ML) $HfSi_2$ sample on clean Si(001) after a 5-min anneal at 750 °C.

(i.e., those with no oxide at the Hf/Si interface) reacted and changed their visual appearance in ~10 min. These samples did not display an ordered LEED pattern after this brief anneal, suggesting that an epitaxial layer was not formed. Moreover, for samples that underwent prolonged annealing, a second feature attributable to SiC appeared at 101.2 eV BE in the Si 2*p* XP spectra [see Fig. 3(a)]. We propose that SiC forms at the bare patches of Si exposed to the residual gases, which is not unexpected for these annealing times, temperatures, and background pressures. Note that since SiC is known to form clusters on Si surfaces,[20] the presence of a LEED pattern would not be significantly affected by the SiC formation.

For the thick films, we may infer a little of the morphology of the reacted layer by examining the LEED pattern shown in Fig. 2. Streaking along the (00) to {01}-like and {10} to {11}-like directions indicates that the exposed patches of substrate are long (compared to the electron coherence length) in one dimension, and short in the other. Thus, the exposed substrate patches must be long and narrow, and must be influenced by the substrate crystallographic template. This is supported by the AFM data.

For thin Hf films, the clean Si(001)-(2×1) pattern emerged after short anneals to only 750 °C; no modification (e.g., streaking) of the bare substrate LEED pattern was observed. However, the “bare patches” in the thin film experiment would be expected to be much larger than in the thick-film experiment, likely larger than the LEED electron coherence length. No streaking would be expected under those conditions.

Many other transition metal silicides form three-dimensionsal clusters on Si surfaces.[23] Although the islanding behavior seen here for hafnium silicides is not surprising in that light, it has not been previously reported to our knowledge. Previous studies[8,10–13,24] have made no mention of islanding. In particular, Galakhov *et al.*[24] interrogated similar samples (Hf thicknesses of 50–200 nm) with depth-dependent, electron-induced x-ray emission spectroscopy (XES). Upon annealing to 780 °C for 30 min, the Hf film was seen to convert to $HfSi_2$ (as expected), but no signal from the Si substrate was evident (for low electron excitation energies). This does not conflict with our findings, as we do not see a LEED pattern emerge (from thick-film samples) until after annealing to 1000 °C. We do, however, have evidence for islanding at lower temperatures (750 °C) in the case of thin (~ML) films. Thus, the picture that emerges is that a thermodynamic driving force exists for three-dimensional clustering of $HfSi_2$ films, but kinetic barriers associated with mass transport have prevented its previous observation. The barrier may be overcome by sufficient annealing temperatures (in the case of thick films) or may be lowered by eliminating the need for so much mass transport (in the case of ML films). Moreover, we have shown that the presence of an interfacial oxide layer significantly slows the kinetics of Hf/Si interdiffusion.

Unfortunately, the change in surface morphology (i.e., islanding) observed upon high-temperature reaction is unfavorable for the intended eventual formation of a uniform hafnium silicate layer having a small Hf/Si ratio by oxida-

tion of a $HfSi_2$ layer. However, no LEED spots were observed from the samples that completely reacted in 10 min, so it may be possible to limit the kinetics of the island formation using, e.g., rapid thermal processing.

The BE of the Hf and Si core levels change little upon reaction to form $HfSi_2$. It is tempting to try to interpret BE shifts in XPS as arising (primarily) from charge transfer between atoms. In the present case, the Hf $4f_{7/2}$ line shifts 0.35 eV to deeper BE, while the Si $2p_{3/2}$ line barely shifts at all. If one attempts to interpret these shifts as stemming from charge transfer, it is difficult to understand why so little BE shifting occurs. One expects that Hf, which has a Pauling electronegativity of 1.3, would donate charge to Si, which has a Pauling electronegativity of 1.9; this should result in a substantial shift to deeper BE for Hf and a shift to shallower BE for Si. However, this simple model is not reliable. In particular, it has been shown that it is unable to account for BE shifts upon alloy and compound formation.[25] Our results for BE shifts are similar overall to the findings of Zaima *et al.*,[12] but differ in detail. They report a Hf $4f_{7/2}$ BE shift from 13.8 eV (for the deposited Hf metal) to 14.1 eV upon formation of $HfSi_2$, which (except for a 0.5 eV absolute discrepancy) is consistent with our reported shift. However, they report a Si $2p_{3/2}$ BE shift from 99.3 eV for bulk Si to 99.1 eV after reaction, presumably to $HfSi_2$. We do not observe this 0.2 eV shift to shallower BE for the Si core level.

CONCLUSIONS

Thick Hf films react with Si(001) to form $HfSi_2$ at 1000 °C, regardless of any initial SiO_2 layer on the Si substrate. An interposing SiO_2 layer, however, will considerably slow the kinetics of the reaction. The resultant $HfSi_2$ exhibits a sharp, fairly symmetric XPS line shape with BE of the $4f_{7/2}$ core level of 14.65 eV, while the Si $2p$ levels exhibit negligible BE shift upon reaction. The resultant film exhibits a pronounced tendency to form three-dimensional islands, leaving patches of the substrate denuded of Hf. The shape of the bare patches is long and narrow, indicating that the underlying crystal structure influences the formation of the islands. For thin (~ML) Hf films on clean Si(001), the reaction and $HfSi_2$ island formation takes places at temperatures as low as 750 °C, consistent with a lower degree of mass transport required.

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*Author to whom correspondence should be addressed. Electronic address: plyman@uwm.edu

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