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M. C. Zeman, C. C. Fulton, G. Lucovsky, et al.



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Thermal stability of TiO_2 , ZrO_2 , or HfO_2 on Si(100) by photoelectron emission microscopy

M. C. Zeman, C. C. Fulton, G. Lucovsky, and R. J. Nemanich^{a)} Department of Physics and Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-8202

W.-C. Yang

Department of Physics, Dongguk University, Seoul 100-715, Korea

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The thermal stability of thin films (3 nm) of transition-metal (TM) oxides (TiO₂, ZrO₂, and HfO₂) grown on ultrathin (~0.5 nm) SiO₂ buffer layers on Si(100) surfaces was investigated with ultraviolet photoelectron emission microscopy (UV-PEEM). The decomposition of the TM oxides was observed in the PEEM during ultrahigh-vacuum annealing at temperatures of ~870, ~900, and ~1000 °C for the TiO₂, ZrO₂, and HfO₂, respectively. Following the decomposition reaction, atomic force microscopy measurements of the annealed surfaces revealed a high density of islands in the decomposed regions. The degradation of the TM oxide films is attributed to a reaction occurring at defects at the TM oxide/SiO₂/Si interfaces, which forms SiO species. Once a portion of the interfacial SiO₂ layer is desorbed as a result of this reaction, Si from the substrate can diffuse into contact with the TM oxide layer, resulting in the formation of a TM silicide and the evolution of SiO. This process continues until the entire TM oxide layer is consumed and only silicide islands remain. © 2006 American Institute of Physics. [DOI: 10.1063/1.2163984]

I. INTRODUCTION

The task of identifying a suitable replacement dielectric for high-performance low-power devices is complex with many challenges. The primary aim in choosing a replacement for SiO_2 is to reduce the tunneling current through the gate oxide of a field-effect transistor (FET) while maintaining the channel charge density. Transition-metal (TM) oxides have received much attention due to their large dielectric constants and relatively large band gaps.^{1–4}

A necessary characteristic of a replacement gate dielectric is chemical and thermal stability with respect to the Si substrate when subjected to various processing conditions. A typical complementary metal-oxide semiconductor (CMOS) process includes a 900–1000 °C dopant drive-in activation anneal during which the gate dielectric must not undergo significant chemical changes or interfacial reactions. X-ray-diffraction measurements of TiO₂, ZrO₂, and HfO₂ films grown at room temperature display a pattern typical of amorphous or nanocrystalline structure. However, during annealing to >600 °C crystalline domains grow in the TM oxide films.^{5,6}

Multiple studies have explored the high-temperature stability of TM oxides, particularly ZrO_2 and HfO_2 .^{4,7–10} It has been reported that ZrO_2/SiO_2 (HfO_2/SiO_2) bilayers on Si(100) substrates become chemically unstable in high vacuum at temperatures ranging from 900 to 1000 °C. Copel *et al.* reported on the annealing of an ~4 nm ZrO_2 layer grown on 1.5 nm of SiO₂.⁷ Following an anneal at 900 °C, medium-energy ion scattering (MEIS) indicated little change in the film composition. However, following a 1000 °C anneal for 30 s, MEIS indicated evidence of silicide formation, and cross-sectional high-resolution transmission electron microscopy (HRTEM) revealed that the film had decomposed into islands. Fulton *et al.* reported on the decomposition of a 3.5 nm ZrO₂ layer grown on a 0.5 nm SiO₂ buffer layer.⁴ X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) spectra were obtained following an ultrahigh-vacuum (UHV) anneal to ~900 °C and indicated the formation of Zr silicide.

Similarly, Muraoka⁸ and Watanabe and Ikarashi⁹ found evidence of interfacial reactions after annealing ZrO₂/SiO₂/Si stacks at 920 and 900 °C, respectively. TEM data obtained by Muraoka showed evidence of islanding after annealing a 2 nm ZrO₂ film on 3 nm of SiO₂ at 920 °C for 1 min. Energy dispersive x-ray spectroscopy confirmed that the islands were ZrSi₂. Watanabe and Ikarashi found that 1-2 nm ZrO₂ films grown on 0.6 nm of SiO₂ partially decomposed during a 10 min anneal at 900 °C to form ZrSi₂ islands as evidenced by XPS and atomic force microscopy (AFM) measurements. The film decomposition was attributed to void nucleation at defects in the oxide bilayer, whereby the migration of Si atoms from the substrate to the defects results in the formation and subsequent desorption of SiO species. This effect leads to the lateral growth of voids in the bilayer, and the remaining Zr forms silicide islands.

In this study, ultraviolet photoelectron emission microscopy (UV-PEEM) is employed to directly observe the thermal decomposition of TiO₂, ZrO₂, and HfO₂ layers (3 nm) on ultrathin (\sim 0.5 nm) SiO₂ buffer layers on Si(100) during high-temperature annealing under ultrahigh-vacuum conditions. The *real-time* capability of PEEM allows the surface

^{a)}Electronic mail: robert_nemanich@ncsu.edu

reaction to be imaged, morphology changes to be observed, and the film decomposition time and temperature to be accurately determined. The TM oxides in this study were observed to decompose during annealing at \sim 870, \sim 900, and \sim 1000 °C for the TiO₂, ZrO₂, and HfO₂ layers, respectively. Following the decomposition reaction, the samples were removed from vacuum, and AFM was performed on each surface revealing nanoscale silicide islands.

II. EXPERIMENT

The TM oxide films were deposited on 25-mm-diameter, *n*-type $(4 \times 10^{18} \text{ cm}^{-3} \text{ phosphorous})$ Si(100) substrates. The as-received Si substrates were loaded into an UHV remote plasma-enhanced chemical-vapor deposition (CVD) system for oxygen plasma hydrocarbon removal and plasma CVD growth of an ~ 0.5 nm layer of SiO₂. The thickness of the ultrathin SiO₂ layer has been verified previously by comparing the relative XPS intensities of the Si and SiO₂ peaks. There was no wet chemical cleaning process prior to loading the substrates, and the base pressure of the oxygen plasma system was $<1 \times 10^{-8}$ Torr. The SiO₂ buffer layers were grown with the substrates at room temperature, a gas flow of 10 standard cubic centimeter per minute (SCCM) of O2 and 50 SCCM of He, and an operating pressure of 60 mTorr He/O₂. The remote plasma was excited with 20 W of inductively coupled rf power.

The substrates were then transferred in air to an UHV oxide molecular-beam deposition (MBD) system (base pressure of $<1 \times 10^{-9}$ Torr) for growth of the TM oxide layers. The Ti, Zr, and Hf metals were evaporated using an electronbeam source, and the rate was monitored with a quartzcrystal oscillator. The films were deposited at ~ 0.5 Å/s in an oxygen ambient of 2×10^{-6} Torr at room temperature. The approximate oxide film thickness was determined from the thickness of the deposited metal layer using the molar densities and the molar masses of the Ti, Zr, or Hf metal and the respective TM oxide. This analysis assumes a ratio of 1.96:1 (oxide:metal) for the thickness of a TiO_2 film formed from Ti metal and 1.56:1 and 1.63:1 for the thickness of Zr and Hf oxide films formed from Zr or Hf, respectively. This approach, which assumes complete oxidation of the deposited TM layer, was corroborated with XPS from the relative intensity reduction of the Si bulk peak of the Si 2p core-level spectra as a function of film thickness.

The annealing experiments were completed using an UV-PEEM system (Elmitec) with a base pressure of $<2 \times 10^{-10}$ Torr. The UV light was generated by a 100 W Hg discharge lamp with an upper cutoff energy near 5.0 eV. Details of the UV-PEEM system have been described previously.¹¹ The sample was annealed in the PEEM system by radiative heating from a tungsten filament in conjunction with electron bombardment directed towards the backside of the sample. The temperature was measured with a thermocouple attached to the sample holder, and the sample surface temperature was calibrated with an optical pyrometer. The PEEM images were enhanced with a microchannel plate and displayed on a phosphor screen. All of the images were ob-



FIG. 1. A sequence of PEEM images showing the decomposition of a 3 nm TiO_2 layer deposited on an ~0.5 nm SiO_2 buffer layer on Si(100) during annealing at ~870 °C. Image (a) was obtained immediately after the temperature reached ~870 °C. Images (b)–(f) were obtained as the sample was annealed at ~870 °C for 4, 10, 21, 26, and 34 min, respectively. The field of view in each image is 50 μ m. The black spots visible near the center of each image are artifacts on the PEEM microchannel plate and are not actually on the sample surface.

tained with a DVC-1312-M-fw digital charge-coupled device (CCD) camera and were recorded with a CCD exposure time of 3 s.

Following removal of the samples from the PEEM, the topography of the samples was investigated with AFM. The AFM images were obtained with an Autoprobe CP-R utilizing a Si cantilever with a spring constant of 1.6 N/m and a resonant frequency of 170 kHz.

III. RESULTS

The contrast in the PEEM images presented in this study is a result of a difference between the work function and the photothreshold of the materials on the surface of the sample. For example, Fig. 1 displays a PEEM image sequence of a sample with a 3 nm TiO₂ layer deposited on an ~ 0.5 nm SiO₂ buffer layer on Si(100) annealed continuously at \sim 870 °C. In Fig. 1(a) the emission from the surface is uniform before any signs of the TM oxide decomposition become visible (the dark spots are defects in the microchannel plate and are not surface features). As the oxide layer begins to decompose, bright regions (attributed to nanoscale silicide islands) form and contrast significantly with the surrounding surface [Figs. 1(b)-1(e)]. The TiO₂ layer is expected to have a photothreshold of approximately 8.8 eV, the bare Si sub-strate has a photothreshold of $\sim 5.1 \text{ eV}$,¹² and the TiSi₂ is-lands have a work function of 4.53 eV.¹³ Therefore, since the photon energy of the incident light from the Hg arc lamp is \sim 4.9 eV the electron emission from the regions containing TiSi₂ is significantly greater than that from the areas containing TiO₂ or from the exposed Si substrate. The absorption edge of TiO₂ is at \sim 3.5 eV;^{14,15} however, the film in this study is sufficiently thin (3 nm) to allow the passage of UV photons to the underlying Si. Consequently, the weak emission from the surface prior to the initiation of the decomposition reaction [Fig. 1(a)] as well as from the areas of the sample that have not yet decomposed in Figs. 1(b)-1(e) involves excitation of electrons from the valence band of the Si substrate into conduction-band states which are above the vacuum level of the TiO_2 .

Considering the electron photoemission from the other TM oxide films in this study, the ZrO_2 and HfO_2 layers are expected to have photothresholds of approximately 8.2 and 7.6 eV, respectively.^{2,4} However, both of these oxide layers have band gaps which are larger than the \sim 4.9 eV photon energy cutoff of the Hg arc lamp which is used for the PEEM excitation. Therefore, the incident photons pass through the TM oxide layer and impinge on the underlying Si substrate. The weak emission from the samples prior to decomposition [Figs. 3(a) and 4(a)] is again attributed to excitation of electrons in the Si valence band which are photoexcited into conduction-band states such that they can transit through the SiO₂ and TM oxide for vacuum emission. Prior results have established that the SiO₂ conduction-band minimum is ${\sim}4.8~\text{eV}$ above the Si valence band, and the vacuum level of the TM oxide is near to this level.^{2,4} As the sample is heated and the decomposition reaction occurs, silicide islands form with work functions less than 4.5 eV,^{16,17} resulting in a surface with a lower photothreshold than that of the initial unreacted surface and also lower than that of the exposed Si substrate ($\sim 5.1 \text{ eV}$).

During the annealing of the TiO₂ sample the temperature was increased from room temperature to 700 °C over a period of 22 min. At temperatures above 700 °C, images of the surface were recorded every 5 s for the duration of the experiment. From 700 to 850 °C the temperature was increased in 50 °C increments, each increment lasting an average of \sim 7 min. As the temperature reached \sim 870 °C, initial signs of the TiO₂ decomposition became visible. After annealing at ~870 °C for approximately 20 s, small, irregularly shaped areas having a photothreshold lower than that of the surrounding surface began to appear. As annealing time progressed to 33 min, the low photothreshold regions expanded and eventually combined to cover the entire PEEM field of view. Once the entire visible portion of the surface had transformed, islands were observed on the surface. However, due to the limited intensity of the Hg arc lamp we were unable to obtain high-resolution images of the nanostructures.

The sample was then removed from the PEEM and examined visually. Prior to loading, the sample was uniform and shiny in appearance. After annealing in the PEEM a large area near the center of the sample was cloudy. This variation across the surface is attributed to a temperature gradient from the center of the sample to the edge which is estimated to be about 50 °C. Finally, AFM was performed on the surface [Fig. 2(a)], and the images revealed a dense array of islands.

Figure 3 presents a sequence of PEEM images obtained during continuous annealing of a 3 nm ZrO_2 layer deposited on an ~0.5 nm SiO₂ buffer layer on Si(100). The temperature was slowly increased to 800 °C over ~51 min. At temperatures above 800 °C, images of the surface were recorded every 5 s for the duration of the experiment. The sample temperature was then increased in 50 °C increments lasting ~6 min each to ~900 °C. After remaining at ~900 °C for



FIG. 2. AFM topography images of (a) TiO₂, (b) ZrO₂, and (c) HfO₂ samples after heating and subsequent decomposition in the PEEM. The images display evidence of island formation as a result of the TM oxide decomposition. Each image is $2 \times 2 \ \mu m^2$.

approximately 90 s the initiation of the oxide decomposition reaction became evident [circled area in Fig. 3(a)]. The entire visible portion of the surface had decomposed after approximately 10 min. The boxed region in the figure displays two particles on the sample surface, which we use to establish that the same region is imaged throughout the experiment.

The ZrO_2 decomposition reaction progressed similarly to the TiO₂ reaction. Small, irregularly shaped regions which were bright compared to the surrounding surface appeared and expanded until they combined to cover the entire visible portion of the surface. One difference between the ZrO_2 and the TiO₂ reactions is the formation of elongated regions which were oriented at 90° with respect to one another. This reaction appears to have progressed from the upper right portion of the visible sample surface to the lower left. This is most likely due to a temperature gradient as discussed above. The sample center is apparently located in the direction of the upper right corner of the image.

Following the reaction, islands were visible in the PEEM images of the decomposed region. The sample was removed from the PEEM and was similar in appearance to the TiO_2 surface following the high-temperature annealing. AFM of the surface revealed a dense array of islands [Fig. 2(b)].

The PEEM image sequence in Fig. 4 is of a 3 nm HfO_2 layer deposited on an ~0.5 nm SiO₂ buffer layer on Si(100)



FIG. 3. A sequence of PEEM images showing the decomposition of a 3 nm ZrO₂ layer deposited on an ~0.5 nm SiO₂ buffer layer on Si(100) during annealing at ~900 °C. Image (a) was obtained approximately 4 min after the temperature reached ~900 °C. Images (b)–(f) were obtained as the sample was annealed at ~900 °C for 5.5, 7, 8.5, 10, and 11.5 min, respectively. The field of view in each image is 150 μ m. The circled region indicates the first sign of the decomposition reaction and the square surrounds two particles on the sample surface.



FIG. 4. A sequence of PEEM images showing the decomposition of a 3 nm HfO_2 layer deposited on an ~0.5 nm SiO_2 buffer layer on Si(100) during annealing at ~1000 °C. Image (a) was obtained approximately 1 min after the temperature reached ~1000 °C. Images (b)–(e) were obtained as the sample was annealed at ~1000 °C for 2, 3, 4, and 5 min, respectively. The field of view in each image is 150 μ m. The circled region indicates the first sign of the decomposition reaction and the rectangles surround particles on the sample surface.

during continuous annealing. The sample was annealed to 800 °C over 40 min and no changes were detected. The temperature was then increased in 50 °C increments lasting \sim 5 min each to \sim 1000 °C. At temperatures above 800 °C, images of the surface were recorded every 5 s for the duration of the experiment. Once \sim 1000 °C was reached, the first sign of the oxide decomposition [circled region in Fig. 4(a)] was observed after \sim 75 s. The entire visible region of the surface had decomposed after approximately 5.5 min. The bright spots in the boxed regions are apparently particles on the sample surface.

The HfO_2 decomposition reaction progressed differently from the TiO₂ and ZrO₂ reactions. The bright regions that appeared were less numerous and became larger before they combined together and covered the entire observed area of the sample. Furthermore, a few of the particles on the surface (boxed regions) seemed to act as nucleation centers for the decomposition reaction. In this case, the reaction began in the upper left region of the visible sample surface and progressed towards the lower right, again attributed to the temperature gradient across the sample. This indicates that the sample center is in the direction of the upper left corner of the image.

Once the portion of the HfO_2 layer that was visible in the PEEM was completely decomposed it was removed from the chamber and appeared visibly cloudy, similar to the other TM oxide samples. AFM was then performed, which revealed a dense array of islands [Fig. 2(c)].

IV. DISCUSSION

Tromp *et al.* investigated the decomposition of SiO_2 films on Si(100) at temperatures ranging from ~900 to 1100 °C using cross-sectional TEM.¹⁸ They observed the formation of voids in the oxide layer which occurred during high-temperature annealing cycles. The voids grew laterally as the sample was annealed, while the remaining portions of the film remained at the initial oxide thickness of 30 nm. It was proposed that during annealing, Si from the substrate reacts with the SiO₂ at defects in the oxide or at the interface, forming SiO species which are desorbed from the surface. Continued annealing resulted in the expansion of the voids which was attributed to the migration of surface Si atoms to the void edges and the continuous formation and desorption of SiO. In TEM images a slight depression was observed in the exposed Si substrate regions, which supports the proposed Si surface migration. In our study, the decomposition of the TM oxide/SiO₂ bilayers on Si(100) appears to progress along a similar reaction path.

The Gibbs free energies for SiO₂, TiO₂, ZrO₂, and HfO₂ are listed in Table I and indicate that the metals have a higher oxygen affinity than Si.¹⁹ This affinity suggests that TM atoms can react with the oxygen in the SiO₂, leading to defect formation in the SiO₂ film via bond rearrangement during the TM oxide growth. These defects can then act as nucleation centers for the formation of SiO species resulting in the reduction of the SiO₂ layer. Considering a $ZrO_2/SiO_2/Si$ stack, two reaction steps for oxide bilayer decay have been proposed by Jeon *et al.*:²⁰

$$Si + SiO_2 \rightarrow 2SiO(g),$$
 (1)

$$6\operatorname{SiO}(g) + \operatorname{ZrO}_2 \to \operatorname{ZrSi}_2 + 4\operatorname{SiO}_2.$$
⁽²⁾

In this case, the Si reacts with SiO_2 at defects in the interface forming SiO species which diffuse towards the surface. Once the SiO comes into contact with the ZrO_2 a second reaction takes place yielding $ZrSi_2$ and more SiO_2 .

There exists another possible reaction path that could occur if Si comes into direct contact with the ZrO_2 layer:²¹

$$4Si + ZrO_2 \rightarrow ZrSi_2 + 2SiO(g). \tag{3}$$

The disappearance of the interfacial SiO_2 layer via reaction (1) would allow contact of the ZrO_2 with Si from the substrate. This would lead to reaction (3) which results in silicide formation. Muraoka studied a ZrO_2 (2 nm)/SiO_2 (3 nm) bilayer on Si(100) which was annealed in UHV for 1 min at 920 °C.⁸ Following the anneal, some areas on the sample had become devoid of the oxide layers while other areas appeared unchanged. Cross-sectional TEM images

TABLE I. Gibbs free energies (Ref. 17) in kcal/mol for Si, SiO₂, SiO(g), TiO₂, ZrO₂, HfO₂, TiSi₂, ZrSi₂, and HfSi₂. (Note: na=not available.)

<i>T</i> (K)	Si	SiO ₂	SiO(g)	TiO ₂	ZrO ₂	HfO ₂	TiSi ₂	ZrSi ₂	$HfSi_2$
1000	-7.3	-234.6	-78.4	-245.7	-282.3	-296.2	-55.7	-63.6	na
1100	-8.4	-237.5	-84.5	-248.9	-285.6	-299.8	-59.5	-67.4	na
1200	-9.6	-240.5	-90.6	-252.3	-288.0	-303.6	-63.4	-71.5	na
1300	-10.9	-243.7	-96.8	-255.9	-292.6	-307.5	-67.6	-75.7	na

taken near the edge of the void regions displayed evidence of holes in the ZrO₂/SiO₂ bilayer as well as hollows in the Si substrate. Images obtained from inside the voids on the surface showed that islanding had occurred. The islands were confirmed to be ZrSi₂ by energy dispersive x-ray spectroscopy. A ZrO_2 (20 nm)/SiO₂ (3 nm)-layered structure on Si(100) was annealed in UHV for 6 min at 920 °C. TEM images showed some contrast change in the lower regions of the ZrO_2 film, but the majority of the interfacial SiO₂ layer remained intact and island formation was not observed. Muraoka concluded that the contact of the ZrO₂ layer with SiO molecules (formed as a result of a reaction at the SiO₂/Si substrate interface) was not sufficient to form a silicide. It was determined that the ZrO₂ layer must come into contact with Si from the substrate for silicide formation to occur. Based upon Muraoka's results it is consistent to propose that the decay of the TM oxide films in our study is initiated with reaction (1) occurring at defects at the TM oxide/SiO₂/Si interfaces. Once a portion of the SiO₂ layer is desorbed, Si from the substrate can come into contact with the TM oxide layer resulting in reaction (3). We are suggesting that the reaction process holds true for the three TM oxides in this study and continues until the entire TM oxide layer is consumed and only silicide islands remain.

The formation and subsequent growth of the voids are evident in the PEEM images presented in Figs. 1, 3, and 4 for TiO₂, ZrO₂, and HfO₂, respectively. Initially, the emission from the surface of each sample appeared essentially uniform. Based on prior studies, it is likely that during annealing to high temperatures, the TM oxide films become crystalline. However, this transition was not evident in the PEEM. Once the sample temperature reached \sim 870, \sim 900, or ~1000 °C for the TiO₂, ZrO₂, and HfO₂, respectively, the decomposition reaction began presumably via the formation of voids in the oxide bilayer. These voids grew and gave rise to the bright, low photothreshold regions containing TiSi₂, ZrSi₂, or HfSi₂ on the sample surface. As annealing continued, the voids expanded to cover the entire visible portion of the sample, leaving silicide islands on the surface (Fig. 2). The results for the decomposition of the ZrO₂ layer, in particular, are in direct agreement with a previous XPS/UPS study which indicated that ZrO2 films are unstable on a thin SiO_2 buffer layer during vacuum annealing at ~900 °C.⁴ The films in the study decomposed into a metallic film (most likely ZrSi₂) and AFM images of the decomposed surface displayed a high density of islands.

The HfO_2 sample exhibited a notably different pattern to the decomposition process. The process occurred at higher temperature with few nucleation sites. As is evident in Fig. 4, the debris on the surface of the HfO_2 sample appears to act as nucleation centers for void growth. It is likely that a dust particle or some other form of debris was on the surface of the wafer prior to the oxide growth. This would result in a defect in the oxide bilayer which could possibly be a nucleation center for a void. Apparently, the clean regions of the $HfO_2/SiO_2/Si$ interface are more stable to the initial defect formation that would initiate the decomposition process.

The variation in decomposition temperatures for the three samples can be explained using the data in Table I.

 HfO_2 has the lowest (most thermodynamically favored) Gibbs free energy of the three TM oxides, followed by ZrO_2 , and then finally TiO₂. Therefore, as the annealing temperature increases, we expect that the TiO₂ film should decompose before the other TM oxides in this study.

V. CONCLUSIONS

The thermal stability of Ti, Zr, and Hf oxides (3 nm) on ultrathin (~ 0.5 nm) SiO₂ buffer layers on Si(100) substrates was investigated in real time with UV-PEEM while annealing at high temperatures. During annealing we observed the decomposition of the TM oxides and the formation of silicide islands.

Our findings indicate that under UHV conditions TiO₂, ZrO₂, and HfO₂ films decompose at ~870, ~900, and ~1000 °C, respectively. The results are consistent with a model whereby the decay of the oxide bilayers (TM oxide/ SiO₂) is initiated with a reaction occurring at defects at the TM oxide/SiO₂/Si interface which produces SiO species. Once a portion of the interfacial SiO₂ layer is desorbed, the Si from the substrate can diffuse into contact with the overlying TM oxide layer resulting in the continuous formation of TM silicide and desorption of SiO. This results in the formation and subsequent growth of voids in the oxide bilayer until the layer is completely consumed and only silicide islands remain.

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