1 Thin film solid-state reactions forming carbides as contact materials 2 for carbon-containing semiconductors

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10 Metal carbides are good candidates to contact carbon-based semiconductors (SiC, diamond, and
11 carbon nanotubes). Here, we report on an *in situ* study of carbide formation during the solid-state
12 reaction between thin films. The solid-state reaction was examined between 11 transition metals (W,
13 Mo, Fe, Cr, V, Nb, Mn, Ti, Ta, Zr, and Hf) and an amorphous carbon layer. Capping layers (C or
14 TiN) of different thicknesses were applied to prevent oxidation. Carbide formation is evidenced for
15 nine metals and the phases formed have been identified (for a temperature ranging from
16 100 to 1100 °C). W first forms W_2C and then WC; Mo forms Mo_2C ; Fe forms Fe_3C ; Cr first forms
17 metastable phases Cr_2C and Cr_3C_{2-x} , and finally forms Cr_3C_2 ; V forms VC_x ; Nb transforms into
18 Nb_2C followed by NbC; Ti forms TiC; Ta first forms Ta_2C and then TaC; and Hf transforms into
19 HfC. The activation energy for the formation of the various carbide phases has been obtained by *in*
20 *situ* x-ray diffraction. © 2007 American Institute of Physics. [DOI: 10.1063/1.2561173]

22 I. INTRODUCTION

23 Several carbon-based semiconductors are promising ma-
24 terials for electronic applications. SiC and doped diamond
25 are superior wide-band-gap semiconductors, offering a high
26 breakdown voltage, high thermal conductivity, small dielec-
27 tric constant, and excellent radiation hardness.^{1,2} Carbon
28 nanotubes (CNTs) are quasi-one-dimensional molecular
29 structures with semiconducting or metallic properties, which
30 are widely investigated for application in the field of
31 nanoelectronics.³ To take advantage of these promising prop-
32 erties, there is a need for reliable contacts to these carbon-
33 containing semiconductors.

34 In silicon-based technology, metal-silicon compounds
35 (silicides) are now widely used as contact materials, since
36 they offer several advantages as compared to metal contacts.
37 Firstly, unlike pure metals several silicide phases are thermo-
38 dynamically stable in contact with silicon. Secondly, when
39 silicides are formed by a solid-state reaction between metal
40 and Si, contact formation can be achieved by means of a
41 self-aligned process (SALICIDE).⁴ The solid-state reaction
42 between the thin metal film and Si only occurs in those re-
43 gions of a patterned substrate, where the metal is in direct
44 contact with the Si (or C for the present case of carbides).
45 Therefore, there is no need for alignment and lithographic
46 patterning of the metal film, since the formation of the sili-
47 cide will be automatically restricted to the contact region.
48 One can expect the same advantages when using carbides to
49 contact carbon-based semiconductors.

50 Carbides (i.e., metal-carbon compounds) are well known

due to some of their unusual physical and chemical proper-
ties. The extreme hardness⁵ and high melting point make
carbides attractive materials for cutting and grinding tools,
but they are also researched as potential catalysts.^{6,7} Table I
gives some basic properties of the carbide phases relevant to
this work. The first column gives the resulting thickness for
the carbide phase obtained when starting from 1 nm of metal
to form the phase (i.e., a measure for the carbon consump-
tion). The thicknesses were calculated⁸ using the x-ray dif-
fraction (XRD) densities,⁹ crystal structure, and number of
atoms. Other properties given are the crystal structure, the
melting point, the formation enthalpy, the resistivity, the ther-
mal expansion coefficient, and the Young's modulus.

The fact that these hard materials are also electronic con-
ductors has more recently led to a research interest on mi-
croelectronic applications for carbides.¹⁰ For instance,
Schaper *et al.*¹¹ have reported on the role of iron carbide in
the growth of multiwalled CNTs. Examples of carbides used
as contact materials are already available in the literature:
WC was examined as a schottky contact to 6H-SiC (Ref. 12)
and to diamond;¹³ TiC was used as an Ohmic contact to
6H-SiC,¹⁴ but also as an Ohmic contact to diamond¹⁵ and
CNTs.¹⁶

Contact materials are usually evaluated on (a) their ther-
modynamic stability in contact with the semiconductor, (b)
their electric conductivity (as high as possible), (c) their for-
mation temperature (as low as possible), and (d) their contact
resistance (as low as possible). Adhesion and mechanical
properties of the contact material and thermal expansion mis-
match between contact and substrate, should also be consid-
ered in the evaluation of contact materials. Therefore, the
thermal expansion coefficient and Young's modulus of the
different carbide phases are listed in Table I.

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TABLE I. Literature overview of the basic properties of the different carbide phases. The carbide thickness was calculated from crystallographic data, using the method described by Chen (Ref. 8). The melting points (MP), the formation enthalpies, the resistivities, thermal expansion coefficients, and the Young's modulus were obtained from different sources.

Table with 8 columns: Carbide phase, Thickness (nm/nm metal), Structure, MP (°C), Formation enthalpy (kJ/mole), Resistivity (μΩ cm), Thermal expansion (10^-6/°C), and Young's modulus (GPa). Rows include various carbides like W2C, WC, Mo2C, Fe3C, Cr2C, Cr3C2, VC, Nb2C, NbC, Mn23C6, Mn3C, TiC, Ta2C, TaC, ZrC, and HfC.

aReference 48.
bReference 47.
cReference 49.

84 In this work, 11 carbide forming metals (Ti, V, Cr, Mn,
85 Fe, Zr, Nb, Mo, Hf, Ta, and W) are examined in a solid-state
86 thin film reaction with amorphous carbon. Not all metals
87 form a carbide, when reacted with carbon. From the binary
88 phase diagrams17 we have selected the 11 transition metals
89 listed above, as carbide-forming metals. Existing literature
90 on the formation of carbides using solid-state reactions is
91 limited to annealing times of one hour and more, followed by
92 ex situ measurements.18,19 Although this gives evidence that
93 a certain phase has formed, there is little information on the
94 kinetics of the process. In this work, a technique was used to
95 observe the solid-state reaction in situ, i.e., during annealing.

96 II. EXPERIMENT

97 The 11 transition metal candidates (Ti, V, Cr, Mn, Fe, Zr,
98 Nb, Mo, Hf, Ta, and W) were deposited on a sputter depos-
99 ited amorphous carbon layer of 200 nm on SiO2 wafers. The
100 30 nm metal layers were sputter deposited at a base pressure
101 of 10^-6 mbar. Cr, Mn, and V were also deposited using e-gun
102 evaporation at a pressure of 10^-5 mbar. The samples were
103 first made without a top layer, but in attempts to prevent
104 oxidation, different capping layers were applied: first, a 5 nm
105 C capping layer, and later, 30 nm C or TiN was used.
106 The reaction between a thin metal film and a carbon
107 substrate was investigated using in situ XRD for phase iden-
108 tification and for determining the activation energy Ea, four-
109 points probe for resistance measurements, x-ray photoelec-
110 tron spectroscopy (XPS) for phase composition information,

and Rutherford backscattering spectroscopy (RBS) for con- 111
tamination and thickness measurements. 112
The in situ XRD experiments were performed at the 113
X20C beamline of the National Synchrotron Light Source 114
(NSLS) at Brookhaven National Laboratory. During anneal- 115
ing, the sample is continuously illuminated by an intense 116
beam of monochromatic x rays (λ=0.177–0.180 nm). Dur- 117
ing the measurement, the samples were heated from 118
100 to 1100 °C in a purified He atmosphere, at different 119
ramp rates (from 0.3 to 35 °C/s). Diffracted photons from 120
the sample are continuously detected by an array of photo- 121
diodes covering 14° in 2θ. Acquisition times can vary from 122
100 ms to several seconds depending on the annealing con- 123
ditions. For the standard heating rate of 3 °C/s presented 124
here, a spectrum is taken every 0.5 s. 125

III. RESULTS 126

A. W-C 127

Figure 1 shows a part of the 2θ spectrum when anneal- 128
ing at 3 °C/s to 1150 °C. Around 200 °C, there is a phase 129
change from β-W to α-W. This does not affect the carbide 130
formation, as was confirmed by in situ measurements of 131
solid-state reactions, starting from α-W. One observes a 132
clear phase transition from W [observe the W(110) peak in 133
Fig. 1] to W2C in the temperature range of 920–970 °C. 134
One cannot tell whether this metal-rich carbide phase is the 135
hexagonal phase or the orthorhombic phase, as, respectively, 136
the (110), (002), (111) and the (002), (200), (102) peaks of 137

FIG. 1. *In situ* XRD pattern of 30 nm W on 200 nm C on SiO₂ with 30 nm C capping layer; $2\theta \approx 35^\circ$ to $\approx 61^\circ$, annealed in He atmosphere from 100 to 1150 °C at 3 °C/s.

FIG. 2. *In situ* XRD measurements on a W–C system with 30 nm C capping layer at heating rates of 1 °C/s (a), 9 °C/s (b), and 27 °C/s (c). The lines on the XRD measurements show the shift towards higher temperatures, when the heating rate is increased (full lines for W₂C, dash-dot lines for WC). The bottom figure (d) shows a linear fit to obtain the activation energy, following Eq. (1). From the fit follows $E_a^{W_2C} = 3.74 \pm 0.33$ eV ($R = 0.9952$) for W₂C formation and $E_a^{WC} = 3.23 \pm 0.41$ eV ($R = 0.9932$) for WC formation.

the different crystal types coincide. From 1050 to 1100 °C the metal-rich carbide phase transforms into the hexagonal monocarbide WC. In Fig. 1 the (001), (100), and (101) peaks are identified. Figure 1 shows data for samples with a 30 nm C capping layer. The same experiments were done for samples without a capping layer. The same two carbide phases were found, although the temperature of the phase transitions were slightly higher.²⁰ Both carbide phases have been confirmed with RBS. Bachli *et al.*¹⁹ reported on tungsten carbide formation on polycrystalline diamond, and found the same phase sequence (first W₂C, then WC).

As explained by Colgan and d'Heurle,²¹ the activation energy E_a can be determined from ramped *in situ* measurements, using a Kissinger-like method. To obtain the activation energy, *in situ* XRD measurements are done at different heating rates (1, 3, 5, 9, and 27 °C/s), and for each heating rate, the transition temperature is determined. In our calculations, the maximum of the first derivative of the intensity of the XRD peak was used as the transition temperature. As shown in Fig. 2 for the W–C system, the transition temperature shifts towards higher values, when the ramp rate is increased. This is clearly demonstrated in Fig. 2(c), where the transition from W₂C to WC does not take place in the measured temperature range (100–1150 °C), at a heating rate of 27 °C/s. Using the equation²¹

$$\ln \left[\frac{dT/dt}{T_f^2} \right] = - \frac{E_a}{k_b T_f} + C, \quad (1)$$

with dT/dt the ramp rate, T_f the formation temperature, and k_b the Boltzmann constant, the activation energy can be determined from the slope of the straight line obtained by plot-

ting $\ln[(dT/dt)/T_f^2]$ vs $1/k_b T_f$ for the different ramp rates and the respective transition temperatures. This is shown in Fig. 2(d). In the remainder of this paper, the correlation coefficient (R) will be supplied with the values for the activation energy as an indication for the scatter of the data points from the fitted line, instead of showing every single Kissinger plot. Apart from this statistical error related to the curve fitting, a more important error originates from the temperature registration in each measurement. Because of this, each transition temperature has an error of ± 3 °C, which will give a variation (an error) on the calculated activation energy.

For the W–C system we obtained an activation energy $E_a^{W_2C} = 3.74 \pm 0.29$ eV ($R = 0.9952$) for W₂C formation, and $E_a^{WC} = 3.23 \pm 0.29$ eV ($R = 0.9932$) for WC formation. Bushmer and Crayton²² studied the self-diffusion of ¹⁴C into WC, and obtained an activation energy $E_a^{b.d.} = 3.82$ eV for bulk diffusion, and $E_a^{g.b.d.} = 3.08$ eV for grain-boundary diffusion. The sheet resistance was measured with a four-point probe, and the resistivities $\rho^{W_2C} \approx 114 \mu\Omega \text{ cm}$ and $\rho^{WC} \approx 300 \mu\Omega \text{ cm}$ were obtained, using the calculated thicknesses of 34.8 and 39.4 nm for the metal-rich carbide and the monocarbide, respectively. Romanus *et al.*²³ found values for the resistivity ranging between 100 and 340 $\mu\Omega \text{ cm}$ for different WC–W₂C mixtures.

B. Fe–C

For the Fe–C system, Fig. 3 shows the formation of the Fe₃C carbide in a temperature range of 550–590 °C. The same experiments were performed on samples with a capping layer. As remarked above, the transition temperature

FIG. 3. *In situ* XRD pattern of 30 nm Fe on 200 nm C on SiO₂, $2\theta \approx 47^\circ$ to $\approx 71^\circ$, annealed in He atmosphere from 100 to 1100 °C at 3 °C/s.

FIG. 4. (a) An XPS depth profile of an as-deposited sample. (b) *In situ* XRD pattern of 30 nm Cr on 200 nm C on SiO₂ with a 30 nm C capping layer, $2\theta \approx 35^\circ$ to $\approx 62^\circ$, annealed in He atmosphere from 100 to 1100 °C at 3 °C/s.

(Fig. 4, inset) shows that C has already diffused into the Cr metal layer. Sinclair *et al.*²⁶ showed the same effect using cross-sectional transmission electron microscopy (TEM). Upon annealing they found the formation of the metastable hexagonal Cr₂C phase, followed by a second metastable phase, orthorhombic Cr₃C_{2-x}, and finally the graphitization of amorphous carbon. The orthorhombic metastable Cr₃C_{2-x} phase was first identified by Bouzy *et al.*²⁸ Figure 4 shows the *in situ* XRD patterns for the Cr–C system. The Cr(110) peak disappears between 580 and 620 °C, and we see the formation of a new phase. Additional *ex situ* XRD on a sample quenched at 650 °C evidenced the coexistence of the metastable carbide phase Cr₂C and the oxide CrO₂. At about 740–770 °C the next phase occurs, and can be identified as Cr₃C_{2-x}. Between 900 and 950 °C the formation of the stable Cr₃C₂ phase takes place. The phase sequence that was observed with the *in situ* XRD is the same as reported by Sinclair *et al.*,²⁶ although they did not observe the last phase, the stable Cr₃C₂ carbide. Worth mentioning is the segregation of a graphite layer like in the Fe–C system. However, the segregation here begins at quite a higher temperature: around 930 °C (graphite peak not shown to save space). Sinclair *et al.* also observed the graphite formation for the Cr–C system.

shifts to slightly lower temperatures for samples with a capping layer (510–550 °C). Santaniello *et al.*²⁴ irradiated Fe layers on high-purity pyrolytic graphite with D⁺ beams at temperatures ranging from room temperature to 1100 K (827 °C), and their results suggest a carbide formation around 800 K (527 °C).

We used *in situ* XRD to determine the activation energy for the formation of Fe₃C and found $E_a^{\text{C cap}} = 4.05 \pm 0.83$ eV ($R = 0.9941$) for samples with a 30 nm C capping layer, and $E_a^{\text{no cap}} = 2.9 \pm 0.27$ eV ($R = 0.9898$) for samples without capping layer.

In Fig. 3, a special feature can be observed around 630 °C at $2\theta \approx 61^\circ$. RBS measurements confirmed that a carbon layer on top of the carbide has formed, and it should be stressed that this segregation occurs, even for samples without an as-deposited C capping layer. Santaniello *et al.* report^{24,25} the segregation of a carbon layer on top of Fe films. Sinclair *et al.*²⁶ used trilayered samples, comparable to the samples with a C capping layer used in this study. They studied this graphite-forming behavior, and named it “carbide-mediated graphitization.” Jiang and Carter²⁷ predict this segregation layer theoretically with density functional theory (DFT) calculations. Therefore, we conclude that around 630 °C; a graphite layer on top of the carbide layer has formed with a diffraction peak at $2\theta \approx 61^\circ$ [(004)] [there is also a peak (002) at $2\theta \approx 29^\circ$].

2.2 C. Cr–C

Cr–C is an interesting metallurgical system, as chromium carbides act as strengthening precipitates in steels. One of the differences compared to other systems is already noticeable with the as-deposited sample. XPS depth profiling

FIG. 5. *In situ* XRD pattern of 30 nm Nb on 200 nm C on SiO₂, for $2\theta \approx 35^\circ$ to $\approx 61^\circ$, annealed in He atmosphere from 100 to 1100 °C at 3 °C/s.

251 D. Nb–C

252 When dealing with solid-state reactions to form carbides
 253 from thin films of metal and carbon, oxidation is an impor-
 254 tant factor to control. In Fig. 5, an *in situ* XRD pattern is
 255 shown for 30 nm Nb on 200 nm C, sputter deposited on a
 256 SiO₂ substrate. Around 700 °C the formation of NbO can be
 257 observed, followed by the formation of NbO₂ around
 258 900 °C. The metal peak of Nb is clearly seen at the start of
 259 the experiment. However, upon annealing, the peak shifts
 260 towards lower 2θ values, which means that the d spacing of
 261 the lattice is increased. Because O atoms are diffusing inter-
 262 stitially into the metal lattice, the lattice (and therefore the d
 263 spacing) expands.

264 Figure 6 shows the solid-state reaction for the Nb–C
 265 system with a 30 nm C capping layer. From 690 °C, the
 266 hexagonal Nb₂C phase appears, with its (100), (002), and
 267 (101) peaks at $2\theta \approx 38.8^\circ$, $\approx 42.4^\circ$, and $\approx 44.4^\circ$, respectively.
 268 This phase transition has not so definite boundaries as the

FIG. 6. *In situ* XRD pattern of 30 nm Nb on 200 nm C on SiO₂ with 30 nm of C as capping layer. $2\theta \approx 35^\circ$ to $\approx 49^\circ$, annealed in He atmosphere from 100 to 1100 °C at 3 °C/s.

FIG. 7. XPS depth profiles of Nb–C system annealed to 850 °C, (a) without capping layer and (b) with 30 nm C capping layer.

next transition to the fcc monocarbide, NbC. From 880 to 940 °C, one observes the appearance of the (111) and (200) peaks of the NbC phase, at $2\theta \approx 40.7^\circ$ and $\approx 47.4^\circ$.

The shift of the metal peak in the XRD plot for the uncapped sample is only an indication that oxidation might have occurred, but XPS (or RBS) gives more evidence. Figure 7 shows XPS depth profiles of samples that were quenched at 850 °C, (a) one without and (b) one with a capping layer. Looking at the oxygen concentration of both and combining these results with the XRD measurements, one can easily see that the Nb–C system has formed an oxide (NbO) when the system had no capping layer, and it formed a carbide (Nb₂C) when 30 nm C was applied as capping layer. Even more evidence for the carbide formation can be found in the single spectrum of the C 1s XPS peak. Ramqvist *et al.*²⁹ have shown that when a carbide is formed, the C 1s peak shows a *carbide* peak, shifted towards a lower binding energy, compared to the original C 1s position. They measured this shift for various carbides and concluded that this shift is a consequence of the transfer of electronic charge from the metal to the nonmetal constituent (here: carbon). For the case of Ti–C, they showed a shift of the metal Ti 2p peak towards a higher binding energy, when a carbide is formed. However, if an oxide is formed, the metal Ti 2p peak shifts in the same direction (to a higher binding energy) as when a carbide is formed, albeit over a different energy (depending on the oxide). Compared to that, if C–O bonds would be measured in the layer (C–O compounds are volatile, so difficult to observe), the C 1s peak would shift to a higher binding energy, thus in the opposite direction of when a carbide is formed. It is clear that one should pay close attention when examining solely the metal peak, and it is

FIG. 8. (a) Nb 3d XPS spectra taken from a sample with a carbon capping layer and one from a sample without a capping layer, annealed to NbC and NbO, respectively. The full vertical line marks the position of the neutral Nb 3d_{5/2} peak. (b) C 1s XPS spectra selected out of an XPS depth profile of a Nb–C system with 30 nm C capping layer, annealed to 1050 °C. The full line shows the C 1s peak at its normal position, taken at a depth where no metal was present. The dashed line shows the C 1s peak at its “carbide” position, taken at a depth where C has reacted with Nb.

FIG. 9. *In situ* XRD pattern of 30 nm V on 200 nm C on SiO₂ with a 30 nm C capping layer, $2\theta \approx 40^\circ$ to $\approx 54^\circ$, annealed in He atmosphere from 100 to 1100 °C at 3 °C/s. (b) and (c) show XPS depth profiles of 30 nm V on 200 nm C with a 30 nm C capping layer, annealed to 600 °C (b) and to 1100 °C (c). The insets show the O 1s peak at the depth, marked with a line in the depth profile.

Activation energies for the two formed carbide phases are $E_a^{\text{Nb}_2\text{C}} = 3.01 \pm 0.36$ eV ($R = 0.9797$) and $E_a^{\text{NbC}} = 4.08 \pm 0.37$ eV ($R = 0.9879$), respectively. Guarnieri *et al.*³⁰ and Barzilai *et al.*³¹ observed the same phase formation sequence for a 200 nm Nb layer on a diamond substrate and an 8 μm Nb layer on a graphite substrate, respectively. And although the latter researchers found lower activation energies for the Nb₂C and the NbC formations, namely, $E_a^{\text{Nb}_2\text{C}} = 1.97$ eV and $E_a^{\text{NbC}} = 1.70$ eV, our results are in the same range as many others.^{30,32,33}

E. V–C

Figure 9(a) shows *in situ* XRD measurement for 30 nm V with a 30 nm C capping layer. The V (110) peak seems to split up around 400 °C and gradually moves towards $2\theta \approx 43.5^\circ$ and $2\theta \approx 51^\circ$. These have been identified as, respec-

FIG. 10. In situ XRD measurements on Ta-C system with C capping layer. The peaks of the different phases are identified. The sample was annealed in He atmosphere from 100 to 1100 °C at 3 °C/s.

TABLE II. Experimental results for the carbide phases, formed through solid-state reaction of thin films. The formation temperature Tform was determined from in situ XRD measurements, at the standard heating rate of 3 °C/s. Only the formation temperature for samples with 30 nm C capping layer are given in the table. All carbide phases were formed, starting from samples with 30 nm of metal, except for the Ta-C system (marked with *), for which the thickness was less. The activation energy was calculated from in situ XRD measurements at different heating rates. The resistivity was measured ex situ using a four-point probe on quenched samples. The range of composition (range of comp'n) was estimated from the binary phase diagram.

Table with 5 columns: Carbide phase, Tform (°C), Ea (eV), Resistivity (μΩ cm), and Range of comp'n MCx (0 < x ≤ 1). Rows include W2C, WC, Mo2C, Fe3C, Cr2C, Cr3C2-x, Cr3C2, VC, Nb2C, NbC, TiC, Ta2C, TaC, and HfC.

thinnest metal layer, they observed the phase formation of Ta2C and TaC for 1 h annealing at 800 and 900 °C, respectively.

G. Zr-C

The in situ experiment for the Zr-C system with a capping layer is shown in Fig. 11(a) for 2θ ≈ 35° to ≈ 49°. Around 300 °C a new peak arises at 2θ ≈ 37.3°, which could be the (100) peak of Zr. On the other hand, Zr3O has peaks around the same positions of Zr. The formation of this oxide (Zr2O, ZrO, and ZrO2 do not have those XRD peaks) seems most plausible, as it is unlikely for a certain diffraction peak to appear and disappear again. Also, in the binary phase diagram of the Zr-O system Zr3O is named α3''Zr, indicating its close relationship to α-Zr. The Zr3O seems to disappear again in favor of the metal, which in turn transforms to a next phase with peaks around 2θ ≈ 38.5° and ≈ 44.3°. Around those 2θ values, both ZrO and ZrC have their (111) and (200) diffraction peaks. Therefore, XPS profiling should be used to determine whether an oxide or a carbide has formed. In Fig. 11(b) a depth profile on a sample annealed to 1100 °C is shown, and one can observe the high oxygen concentration in the layer, so the formation of ZrO is most probable. Inspecting the XPS C 1s spectra, a very small shift towards the "carbide" position was observed, as can be seen on the inset of Fig. 11(b), where the shoulder has been marked. We therefore conclude that a small amount of carbide has formed, but that oxidation of Zr was predominant, in spite of the presence of a capping layer.

FIG. 11. (a) *In situ* XRD measurements on Zr-C system with C capping layer. The sample was annealed in He atmosphere from 100 to 1100 °C at 3 °C/s. (b) XPS depth profile on the same sample, after annealing. The inset shows XPS C 1s spectra, where a small peak at the “carbide” position hints some formation of ZrC.

In order to make the current report self-contained, we give an overview of the results, and include the activation energy for the TiC formation.

The Ti-C system is sensitive to oxidation (similar to Nb-C), and the formation of TiC occurred between 550 and 650 °C for samples with a 30 nm C capping layer. An activation energy $E_a = 1.45 \pm 0.81$ eV ($R = 0.7189$) was calculated.

The Mo-C system is less sensitive to oxidation. The transition to the Mo₂C phase was observed between 830 and 900 °C (no capping layer). Different capping layers were used, and the formation temperature varied significantly: $T_f^{5 \text{ nm C}} = 730\text{--}800$ °C, $T_f^{30 \text{ nm C}} = 700\text{--}770$ °C, and $T_f^{30 \text{ nm TiN}} = 750\text{--}830$ °C. An activation energy was obtained for the Mo-C system with a 30 nm C capping layer, $E_a = 3.15 \pm 0.23$ eV ($R = 0.9968$).

IV. DISCUSSION

As mentioned before, the formation of carbides from thin films of metal and carbon is extremely sensitive to oxidation. We found that W, Mo, Fe, Cr, and V form a carbide, even when no capping layer is applied. The others (Nb, Ti, Ta, and Hf), however, need the C capping layer, or an oxide will form, instead of a carbide. As an example, this was discussed for the Nb-C system, and shown in Fig. 5. In Table III the elements are arranged with decreasing electronegativity. The metals last mentioned here (Nb to Hf) have a lower electronegativity compared to, e.g., W and Mo, so they have a greater “natural attraction” towards oxygen (which has an electronegativity of 3.44). So, one expects that these metals have a bigger chance of forming an oxide rather than a carbide. Cr and V are actually in between the two groups (W, Mo, and Fe versus Nb, Ti, Ta, and Hf), which may explain why they tend to first form an oxide, but eventually the carbide phase governs the solid-state transformation. Mn and Zr are exceptions, as we were not able to form a carbide phase for these metals. We must mention that if one would be taking more severe steps to eliminate the presence of oxygen than was done in our work (such as UHV deposition and/or UHV annealing), the necessity of the capping layer might disappear.

When looking at the binary phase diagrams,¹⁷ the first group has carbide phases with a very narrow range of composition (observed as a single vertical line in the phase diagram): W, Mo, Fe, Cr, and Mn. The second group (V, Nb, Ti, Ta, Zr, and Hf) has carbide phases which can be stable within a certain range of carbon concentration. The ranges of composition listed in Table II are estimated from the binary phase diagrams. This broad range of composition of the carbide phase will reflect itself in a change of certain physical properties of the carbide, as C vacancies will act as powerful scattering centers for electrons and phonons. Within the range, there will be a variation of several properties: the lattice parameters and density,³⁵ Hall coefficient,³⁶ transition temperature to the superconducting state,³⁷ coefficient of thermal expansion, magnetic susceptibility, heat of formation, and (technologically important for microelectronics) the

H. Hf-C

The formation of the monocarbide HfC during the anneal of a 30 nm Hf layer with a 30 nm C capping layer, on an amorphous 200 nm C layer, can be seen in Fig. 12. Starting around 710 °C, the (111) and (200) peaks of HfC appear, and around 810 °C the transformation is complete. The capping layer is necessary to form the carbide. From *in situ* XRD measurements at different ramp rates, we have determined the activation energy for the HfC formation as $E_a^{\text{HfC}} = 2.05 \pm 0.19$ eV ($R = 0.9749$).

I. Ti-C and Mo-C

The thin film solid-state formation of titanium carbide and molybdenum carbide is discussed in a previous paper.²⁰

FIG. 12. *In situ* XRD pattern of 30 nm Hf on 200 nm C on SiO₂ with 30 nm of C as capping layer. $2\theta \approx 35^\circ$ to $\approx 49^\circ$, annealed in He atmosphere from 100 to 1100 °C at 3 °C/s.

TABLE III. The transition metals studied in this work, sorted by electronegativity. The phase sequence for the solid-state reaction are listed in order of appearance. The last two columns indicate for which materials a capping layer is absolutely necessary to obtain carbide formation.

Table with 5 columns: Metal, Electronegativity, Phases, TF-Exp without cap, TF-Exp with cap. Rows include W, Mo, Fe, Cr, V, Nb, Mn, Ti, Ta, Zr, Hf.

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resistivity. It is clear that one has to take this into account, when searching for reliable contacts for semiconductors. Considering the kinetics of the reaction, one can learn from literature that the reaction for carbide formation is diffusion controlled, e.g., this was reported for TiC by Peng and Clyne and for Mo2C by Mikahilov et al. Therefore, diffusion of one of the species through the growing film will be the rate-controlling mechanism for the reaction. The graphite formation on top of the carbide layer (for Fe-C and Cr-C) supports the concept that the small carbon atoms are diffusing fast through the metal (or carbide). Woodford and Chang evidenced that carbon is the only species undergoing significant diffusion in the Nb-C system. If one compares the range of composition and the activation energies for the different carbide phases, one would intuitively try to correlate both. One would expect that C atoms will move more easily through a layer with more vacancies, which may explain the lower activation energy. Many authors pose that the activation energy for diffusion is independent of the composition. Others have shown that different carbon diffusion mechanisms are active, and the dominance of a particular mechanism is dependent on the composition and on the temperature range. Due to these different diffusion mechanisms, a variation in the activation energy may occur. Yu and Davis found a different activation energy for single crystals of NbC0.868 and NbC0.834, compared to the activation energy for NbC0.766. This difference was attributed to the presence of a different diffusion mechanism. For NbCx systems with x > 0.766, the carbon atom jumps to a vacant octahedral site in the <111> direction by a two-step process, called the O-T-O mechanism: first, a shorter <111> jump to an unoccupied tetrahedral site on the Nb sublattice, followed by an immediate <111> jump to a vacant octahedral site (i.e., a vacant site on the C sublattice). As the carbon concentration increases, the character of bonding in the material changes, which results in an electronic charge distribution most readily passed by C atoms jumping in the <111> direction. For lower carbon concentrations, the transient divacancy mechanism is favored, where the carbon atom jumps to the vacant octahedral site by way of a normally occupied metal vacancy, which has momentarily become associated with the carbon vacancy.

Overviewing our results for the activation energies, we see that the results for TiC, HfC, VC, Nb2C, Mo2C, and WC are in the same range of the results of Yu and Davis that were correlated to the O-T-O mechanism, while the other results (W2C, Fe3C, and NbC) show higher activation energies that correlate better with the transient divacancy mechanism. However, one would have to look at the charge densities of the different compounds, in order to get an idea of the most favored diffusion path, to correlate the activation energy to a certain diffusion mechanism. We stress, however, that other influences such as grain boundary diffusion probably play a role in the diffusion. Barzilai et al. wrote that the activation energy values for carbon diffusion in thin layers differ greatly from those obtained for bulk materials, and they address their difference in values to the microporosity of the film. It is also well known that the activation energy at grain boundaries (or defects) is different than in bulk material. For carbide formation, the work of Yeh et al. and Hatano et al. give evidence for this difference. So from this all, one can conclude that grain boundaries and dislocations will play an important role in our growth of carbides. Furthermore, the influence of impurities such as oxygen in the (surface) layer, but also nitrogen or other metals, will also have its influence on the diffusion, and hence the activation energy. Matzke writes that defect concentrations are often impurity controlled and that diffusion is governed by impurity-defect interactions. As mentioned in the introduction, several criteria should be used to select the best candidate as electric contact to carbon-containing semiconductors. Firstly, the most carbon-rich carbides are thermodynamically stable in contact with an infinite carbon supply. Secondly, one has to take into account the sensitivity towards oxidation, so W, Mo, Fe, Cr, and V come first to mind as promising candidates. They do not have the necessity of a capping layer, which facilitates the fabrication of the contact. Cr and V first form oxides, which may cause problems when more oxygen is available during processing. From the remaining candidates, Mo2C and Fe3C have relatively low formation temperatures (W2C not), which is quite favorable. However, Fe3C tends to segregate a graphite layer, which may interfere with the device

operation. Mo₂C thus appears as a primary candidate for contacting carbon-containing semiconductors. Our work focused on the formation of carbides. For practical application as a contacting material to carbon containing semiconductors, the electrical nature of the carbide-semiconductor interface will also be important. Unfortunately, the use of amorphous carbon substrates during most of our experiments did not allow for an investigation of the contact resistance. Undoubtedly, the contact resistance will vary depending on the semiconductor that is used (SiC, diamond, carbon nanotubes,...). For contacts to diamond, Nakanishi *et al.*⁴⁶ reported electrical measurements for Mo contacts to boron-doped polycrystalline diamond films. For diamond with a resistivity of 13 Ω cm, they found a contact resistance of ~10⁻² Ω cm² for as-deposited Mo. Annealing of this sample for 60 min at 600 °C resulted in the formation of Mo₂C and in an improved contact resistance of ~10⁻³ Ω cm². For diamond with a resistivity of 0.08 Ω cm, annealed Mo films resulted in a contact resistance of ~10⁻⁶ Ω cm². They also report that the Mo₂C contacts were thermally stable and did not deteriorate after annealing at 600 °C for 3 h.

586 V. CONCLUSION

According to the binary phase diagrams, only 13 transition metals form a stable carbide phase and in this work 11 of these were investigated in their thin film solid-state reaction with carbon. We found that nine of these thin film transition metal-carbon systems (W, Mo, Fe, Cr, V, Nb, Ti, Ta, and Hf) form stable carbide phases through a solid-state reaction with carbon. The necessity of a capping layer for Nb, Ti, Ta, and Hf was discussed. Despite the capping layers, the Mn-C and Zr-C systems did not form carbide phases. The different phases of the solid-state reaction and their transition temperature have been identified using *in situ* XRD, and for some of the phases an activation energy was obtained with kinetic studies, and resistivities of the carbide phases were measured *ex situ*. The results are summarized in Table II. We also mention the unexpected phenomenon of graphite formation on top of the carbide phase, for the Fe-C and the Cr-C systems.

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