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MOCVD of Cr3(C,N)2 and CrSixCy Films Growth and Characterization

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CrCxNy and CrSixCy thin films were deposited under low pressure by metallorganic chemical vapor deposition (MOCVD) in the temperature ranges 380-450°C and 450-500°C, respectively, using Cr(NEt2)4 and CrCH2SiMe34 as single-source precursors.
The growth was achieved in a cold-wall vertical reactor using, respectively, H2 and He as the carrier gases. Both types of films exhibit a mirrorlike surface morphology and are amorphous as-deposited. The CrCxNy layers start to crystallize at 600°C after annealing for 1 h under vacuum, whereas it is necessary to reach 650°C under H2 atmosphere. In both cases, the original ternary phase Cr3(C0.8N0.2)2 crystallizes. The resistivity of as-deposited amorphous CrCxNy films is typically 600. cm, and it decreases to 150 #. cm after annealing upon the formation of polycrystalline Cr3#C,N#2 films. The CrSixCy layers have a very stable amorphous structure until 850°C for 4 h. In spite of their metallic appearance, they exhibit a high resistivity compared to the Cr3#C,N#2 films. The main characteristics of these Cr-based layers is presented and discussed.

The performances and functionalities of integrated circuits have been continuously improved these last years mainly thanks to a higher level of integration. Indeed, the density of devices increases significantly as a result of the major reduction of their dimensions, which was facilitated by the use of copper as interconnection material in replacement of aluminum and its alloys. Indeed, Cu has a lower resistivity #1.67 #. cm compared with 2.65 #. cm for Al#, a greater resistance to electromigration,1 and a lower contact resistance.

However, the high mobility of copper in silicon,2,3 silica,4 and low-k dielectrics involves serious problems, among which are the increase of contact resistance and the degradation of electrical connection. Copper incorporated in silicon creates deep levels in the energy bandgap, which act as generation-recombination centers and decrease the carrier lifetime.5,6 Moreover, when copper diffuses in boron-doped silicon, it can form neutral Cu-B complexes,7,8 which reduce the active boron concentration in silicon. For reliable devices, it is essential to stop the migration of copper in the adjacent layers. Consequently, Cu must be isolated from its environment by a diffusion barrier. Such a thin film must block the diffusion of copper during both the manufacture and the use of the processor. In addition to being copper-tight, an ideal diffusion barrier must be entirely transparent to electrons.9,10

It is generally admitted that the higher the melting point of a material, the weaker the diffusion processes, and consequently the better the barrier properties. Thus, the first conducting materials that were studied as barriers are compounds with a high melting point such as #i. refractory metals,11-13 #ii. their alloys,14 and #iii. the transition metal nitrides.15-18 Indeed, these materials are well known for their good thermal and chemical stability,19 and for their relatively low electrical resistivity. Because of their great similarity with the nitrides, carbides20-23 and borides24 of the same transition metals were also considered. Currently, the efforts focus on the ternary compounds of the type M-Si-N #M = Ti,Ta,W#, which exhibit interesting properties.25,26 Another approach is the use of multilayer structures combining the advantages of various thin film

materials, but this concept is limited because of the complexity of the architectures and of the difficulties to develop reliable processes to deposit ultrathin layers since the total thickness must be maintained at the nanometric scale.27

There are only a few reports on Cr-based thin films for applications as conducting diffusion barriers.28 For instance, the potentialities of PVD metal Cr thin films with a polycrystalline structure12,29 and PVD CrNx layers29,30 were investigated. The chromium carbide Cr3C2 also deposited by PVD was tested as interconnect material.31 Despite the limitation of PVD in high aspect ratio contacts, these Cr-based layers were deposited by this line-of-sight process.

Nevertheless, Cr-based layers can be deposited at low temperature by metallorganic chemical vapor deposition #MOCVD#, which does not exhibit this drawback. Thus, various CrNxCy films can be deposited in this ternary system using metallorganic precursors. For instance, the Cr-N-C system presents a ternary metastable compound Cr3#C0.8N0.2#2,32,33 whose homologs do not exist in the Ti-N-C and Ta-N-C systems. Amorphous thin films of this ternary compound can be deposited by MOCVD using Cr#NEt2#4 as a single-source precursor.32 Interestingly, this compound presents attractive properties for applications as barrier material such as, for instance, #i. a relatively high melting point #1600°C#, #ii. a strong atomic density #1.1 . 1023 atom cm-3#,34 and #iii. a low electrical resistivity.35

Among the ternary systems, it is known that addition of silicon in nitrides of transition metals to form M-Si-N phases increases considerably their crystallization temperature and provides high performance barriers. We assumed in starting this research work that in such ternaries, the substitution of nitrogen by carbon can form original M-Si-C materials with properties related to those found for M-Si-N systems. As a result, in parallel to the Cr-N-C system, we were also interested by the Cr-Si-C system to find new barrier materials. In this family of ternary compounds, we have previously deposited by MOCVD amorphous CrSixCy films using Cr#CH2SiMe3#4 as a single-source precursor.36

In our previous works on MOCVD of CrNxCy 32,35 and CrSixCy,36 the coatings were grown in a horizontal hot-wall CVD reactor. They were deposited on steel substrates with relatively high thicknesses for applications as hard metallurgical coatings. In the present paper, we have developed a vertical cold-wall CVD reactor more appropriate to the growth of thin barriers and that will be used further in sequence for copper metallization. Both previous MOCVD processes were adapted to this new reactor, and Cr-based thin films have been deposited. Preliminary results obtained in this cold-wall reactor were recently reported for the growth of CrNxCy 37 and CrSixCy 38 in an ECS Meeting in Paris, France.

In this paper, details on these deposition processes are described and the influence of the growth conditions on the chemical and structural characteristics of these films are presented and discussed. The behavior of these Cr-based thin films as barrier materials is reported in a companion paper.3

Scheme 1.

Properties of the Molecular Precursors

Properties of Cr(NEt2)4.— In this molecular compound, the chromium atom is bonded to four nitrogen atoms of alkylamido groups #Scheme 1a#. It is a green and viscous liquid at room temperature which is soluble in hydrocarbon solvents. It is monomeric both in solution and in the gas phase, whereas the related derivatives of Mo and W form dimers. Contrary to the Ti and Ta homologs, it is not commercially available. It was synthesized according to the procedure described in the literature.40 It was purified by distillation under reduced pressure. However, it is air sensitive and must be handled under controlled atmosphere in a glove box. It is sufficiently volatile, #3 . 10-3 Torr at 60°C,32 to be vaporized at 50°C and transported using a carrier gas into the reactor under reduced

Figure 1.
TimedependenceofthequantityofprecursorvaporizedduringvariousCVDrunsundertheconditionsgiven intheinserts:#a#Cr#NEt2#4;
#b#Cr#CH2SiMe3#4.Theverticaldottedlineindicatesthemaximumtimeforusingasinglefillingofthesat urator.
Figure 2.
Simulationprofilesof#a#thetemperatureand#b#thegasvelocitycalculatedusingFluent6.0forourvertical cold-wallCVDreactorundertypicalconditions:T=400°C;P=0.1Torr;H2flowrate=5sccm.
pressure. Under the usual conditions of thermogravimetric analysis
#TGA#, it was found stable until #100°C #atmospheric pressure, N2
as carrier gas, heating rate 10°C/min#.

From several measurements of the weight loss of the bubbler after CVD runs for different periods, we have determined a mean evaporation rate of 0.76 mg min-1 #Fig. 1a#. This typical value corresponds to a molecular flow rate of 2.24 #mol min-1 or 0.05 standard cubic centimeters per minute #sccm#. Figure 1 shows that the vaporization rate is approximately constant until 500 min when a single load is used in the thermostated bubbler. For longer times using the same filling of the saturator, the precursor progressively decomposes and loses its volatility, likely due the combined action of heating of the bubbler #50°C. and the vigorous stirring induced
by the bubbling of the carrier gas.

Properties of Cr(CH2SiMe3)4.— The molecular structure of this precursor is shown in Scheme 1b. The metal is bonded to four carbon atoms and then it is formally a Cr#IV. atom. It is a crystallized solid that exhibits an indigo color. As the previous metallorganic
complex, it is not commercially available and was synthesized according to the experimental procedure previously reported.41 Its melting point is relatively low #39-40°C#, and it has a sufficient volatility #5.2 . 10-3 Torr/25°C36. to be vaporized and transported
in the gas phase using a saturator and a carrier gas. It is also particularly sensitive to oxygen and moisture and, as a result, it was handled in a glove box under argon atmosphere.

Figure 1b shows the relatively good behavior of this precursor
when the saturator is heated at 38°C. At this temperature, the sublimation rate was found constant for more than 11 h using only one
filling of the saturator. Beyond this period, the sublimation rate decreases. This change in the vaporization rate is partially due to a
beginning of decomposition because dark solid residues were observed in the saturator after long CVD runs. However, the main
origin is the continuous change of the surface area of the solid in
contact with the carrier gas due to the consumption of the precursor.
Typically the sublimation rate is 0.48 mg min-1, which corresponds
to a molecular flow rate of 1.20 #mol min-1 or 0.027 sccm.

Experimental

The thin films were deposited in a vertical quartz cold-wall CVD reactor #50 mm in diameter#. The samples were placed on a SiCcoated graphite susceptor #35 mm in diameter#. This sample holder was heated by induction and the temperature was controlled by a thermocouple inserted in its heart. The total pressure was regulated independently of both the atmosphere and the total flow rate using an automatic system constituted by a butterfly valve coupled to a

Baratron gauge. Additionally, an IR pyrometer was used to control the surface temperature of the substrates and also to study in situ the early stages of the growth process as recently reported.42

The saturator was filled with the molecular precursor in a glove box under inert atmosphere to avoid any contamination and degradation. The saturator was heated by a thermostated bath. The gas flows #He, H2. were regulated using mass flow controllers. The vapor of a precursor transported by the carrier gas was introduced into the reactor through a shower head located at approximately 5 cm above the substrates. The decomposition by-products at the outlet of the reactor were trapped in a liquid nitrogen trap to protect the pumping system and for further analyses if required.

To validate the reactor geometry, a simulation of the hydrodynamic flows and fields of temperature was carried out using the code Fluent 6.0. Figure 2 presents the gas velocity and the temperature profiles obtained under typical deposition conditions. Under our CVD conditions, it can be seen, for instance, that when the substrates are heated at 873 K, the gas phase is significantly heated only in the immediate vicinity of the susceptor. This avoids premature gas phase decomposition and allows a better control of surface reactions. The shower head remains close to the ambient temperature. The gas velocity reveals a quasistagnant boundary layer above the surface of the susceptor. A uniform diffusion of gaseous reactives through this boundary layer is desired for good control of the deposition rate. This is a key point of the process because uniform and very thin thicknesses are necessary for barrier applications. No evidence of recirculation loops, which could be detrimental for the film quality, was observed under the explored conditions.

Three types of substrates #2 . 2cm. were used: #i. Si#100. wafers, #ii. thermal SiO2 #500 nm thick. grown on Si#100#, and #iii. patterned thermal silica #750 nm thick. on silicon with trenches of different aspect ratios. Prior to the deposition, they were degreased 10 min in boiling trichloroethylene, then 10 min in hot acetone, and rinsed in distilled water. The silicon substrates were etched in a diluted HF solution to remove the native oxide. After the cleaning procedure, they were rapidly placed into the CVD reactor and three vacuum-pressurization #H2. cycles were performed before being pumped under high vacuum for several hours ##10-6 Torr#.

Identification of the crystalline phases and determination of their structure were performed by grazing incidence #2°. X-ray diffraction #XRD, Cu K##. The film composition was estimated by X-ray photoelectron spectroscopy #XPS. and electronic probe microanalysis #EPMA. for the thicker films. The profiles of the elements constituting the layers were analyzed by secondary ion mass spectrometry #SIMS. and Rutherford backscattering #RBS#. The electrical resistivity was measured at room

temperature using a four-points probe.
The film thickness was determined with a profilometer after sputter etching the film until the interface with the substrate by SIMS.

Results and Discussion

Study of the growth.— The MOCVD conditions used for the growth of the Cr-based films are reported in Table I. The variation of the thickness of CrCxNy films as a function of the deposition time reveals the absence of an induction period whatever the substrates, Si#100. or SiO2 #Fig. 3a#. By contrast, an induction period of several tens of minutes was observed for the growth of CrSixCy on SiO2, whereas the growth of this film starts immediately on Si#100. substrates #Fig. 3b#. The thickness dependence on the deposition time is relatively linear for the two types of Cr-based layers, revealing a constant growth rate.

Thus, the deposition rate was determined by dividing the film thickness by the effective growth duration. Figure 4 shows the Arrhenius plots of the growth rate of CrCxNy and CrSixCy films on Si#100. substrates as a function of the deposition temperature. For CrCxNy films, the growth starts at a temperature as low as 380°C and the rate is thermally activated, indicating that the process is likely controlled by the kinetics of the surface reactions. Indeed, an apparent activation energy of approximately 77 kJ mol-1 was deter-

Figure 3.
Influenceofthedepositiontimeonthethicknessofthefilmsgrownon###Si#100#and###SiO2/Sisubstrates:#a#CrCxNy and#b#
CrSixCy layers.
Figure 4. ArrheniusplotofthegrowthrateofCrCxNy andCrSixCy filmsdepositedonSi#100#substrates.

G654 Journal of The Electrochemical Society, 152 #8. G651-G659 #2005.

Figure 5.
XRDpattern#grazingincidence2°#ofathinfilmgrownbyMOCVDusingCr#NEt2#4underheliumatmosphereshowingtheformationofthecubicphaseCrNonaSi#100#substrate.

mined, which is in the typical range 50-100 kJ mol-1 reported in the literature as characteristic of a kinetically controlled regime.43 At this stage, we have to keep in mind that a kinetic regime is the best mode to get uniform step coverage on nonflat surfaces. Thus, the CVD conditions of this process seem favorable for the growth of thin barriers. It can be noted that the apparent activation energy found is significantly lower than the energy required for the breaking of the chemical bonds of Cr#NEt2#4 molecules if the decomposition occurred in the gas phase by homolytic fission #radical mechanism#. As a result, the precursor undergoes essentially a heterogeneous decomposition where the surface probably plays a significant role. A similar dependence of the growth rate with the temperature was found for the deposition of CrCxNy films on SiO2 substrates #data not represented#. The apparent activation energy determined on SiO2 is about 78 kJ mol-1, which is the same value as on Si#100. taking into account the uncertainty.

The temperature range of deposition of CrSixCy films is substantially shifted towards higher temperatures because of the greater thermal stability of Cr#CH2SiMe3#4 compared to Cr#NEt2#4. The deposition starts at 400°C and the growth rate increases continuously until 500°C. However, it seems that a change in the slope is observed around 450°C, with probably a kinetically controlled regime below this temperature. An apparent activation energy of approximately 110 kJ mol-1 was roughly estimated, which is appreciably higher than using Cr#NEt2#4 as a precursor. However, this

Table I. MOCVD growth conditions of the two types of Cr-based thin films.

Conditions	Cr3#C,N#2	CrSixCy
Precursor	Cr#NEt2#4	Cr#CH2SiMe3#4
Vaporization temperature #°C.	50	35-38
Growth temperature #°C.	400-420	475-500
Total pressure #Torr.	0.1	0.5
Carrier gas #sccm.	H2 #5.	He #10.
Mole fraction #%.	0.99	0.28
Precursor flow rate #sccm.	0.05	0.027
Precursor molecular rate ##mol min-1.	2.2	1.2
Substrates	Si#100#;SiO2/Si	Si#100#;SiO2/Si
Growth rate #nm/min.	0.8-3.5	0.3-1.5

Figure 6. SIMSdepthprofilesofas-depositedCr-basedlayers:#a#CrCxNy grownat400°ConSi#100#and#b#CrSixCy grownat475°ConaGe#100# substrate.TheGetracewasoffsetforclarity.

remains in the typical range for heterogeneous reactions, and is in

agreement with the higher stability of Cr#CH2SiMe3#4.

Interestingly, in the temperature range 400-450°C that is common to both CVD processes, the deposition rate of CrCxNy is approximately four times higher than that of CrSixCy. This is explained in large part by the higher mole fraction of Cr#NEt2#4 but there is only a factor of two difference with the mole fraction of Cr#CH2SiMe3#4 #Table I#. As a result, the decomposition reactions and subsequently the growth rate are certainly faster using Cr#NEt2#4.

Structure and composition.— SEM observations have shown the highly smooth surface morphology of the two types of layers in good agreement with their mirrorlike and metallic appearance. Their structure is very dense. The surface roughness is in the range 0.5-4 nm depending on the CVD conditions and the film thickness.

The XRD patterns of as-deposited CrCxNy films exhibit a broad hump centered at 21° as shown, for instance, by the reference pattern in the stacking of Fig. 8a. This probably reveals a structural order at the nanometric scale. The XRD patterns of as-deposited CrSixCy layers are featureless, indicating that the films are amorphous #see, for instance, the reference pattern in the stacking of Fig. 11#. As expected, this is likely due to the incorporation of silicon into the films, which contributes to the amorphization. The structural transformation of these films upon annealing and the abovementioned figures are detailed and discussed in the next section.

Table II. Chemical composition of as-deposited CrCxNy films determined
by EPMA compared to typical values of the ternary
phase Cr3,,C,N…2 reported in the literature.34,44-46

Deposition Atomic composition
temperature
Sample #°C. Cr C N

Cr35 400 52 35 13
Cr37 400 53 34 13
Cr38 420 52 36 12
Cr3#C,N#2 -60 30-32 8-10

Except when otherwise specified, the CrCxNy films were deposited using H2 as carrier gas #Table I#. However, because He was
used as carrier gas in our previous work,32 it was also used in preliminary MOCVD runs with this cold-wall reactor. Then, it is noteworthy that when using He as carrier gas, polycrystalline thin films
with the CrN cubic structure were obtained #Fig. 5#. This contrasts
with the results from the decomposition of Cr#NEt2#4 in a horizontal
hot-wall CVD reactor under He atmosphere since amorphous layers
were obtained and the cubic nitride was never observed.32,35

Gas-phase reactions certainly play a major role in isothermal
reactors using Cr#NEt2#4 by producing intermediate reactives which
undergo further decomposition to form amorphous CrCxNy films
with a low nitrogen content. Under these conditions, a decomposition mechanism of this family of precursor has been proposed.33

The decomposition mechanism of Cr#NEt2#4 in a vertical coldwall reactor is likely different since gas-phase reactions are minimized in favor of heterogeneous reactions. As a result, CrN is
formed using the same reactive gas mixture, i.e.,Cr#NEt2#4 and He
as carrier gas. In the cold-wall reactor and under He atmosphere,
nitrogen incorporation into the film is facilitated to the detriment of
carbon. This is probably because the nutrient species have an N/Cr
atomic ratio close to four, the value of the starting molecule. Indeed,
the N/Cr ratio of species originating from gas-phase decomposition
is certainly significantly lower than four due to the release of
N-containing molecules that do not participate in the growth of the
film.33

We have observed that rapid addition of H2 or using directly H2
as carrier gas in the cold-wall reactor changed the decomposition
mechanism to form amorphous layers very similar to those previously obtained in the hot-wall reactor using He as carrier gas. Hydrogen is known to be very reactive in the presence of metal surfaces during the growth on which it can adsorb dissociatively. This
strong reducing agent would contribute to form intermediate reactives that would facilitate the carbon incorporation detrimentally to
nitrogen that would be removed from the surface to the gas phase as

gaseous by-products, as induced by gas-phase reactions in the hotwall reactor. Obviously, the intermediate reactives are probably not
the same as in the isothermal reactor under He atmosphere.

SIMS analyses #Cs+ ions bombardment. reveal the homogeneous distribution of the principal elements until the interface with the substrate for the two types of Cr-based films. Typical SIMS depth profiles of CrCxNy and CrSixCy layers are presented in Fig. 6. In spite of maximum precautions to handle both molecular precursors and to purge the CVD reactor prior to the growth, a very thin oxidized interphase was frequently observed for the two types of Crbased layers at the interface with the substrate. For CrCxNy, this was
recently demonstrated by in situ and real time analysis of the early stages of the growth using IR pyrometry.42 More efficient purges of the CVD reactor limited this oxidation since this oxidized interphase was undetectable by using IR pyrometry as an in situ diagnostic tool.42 A further improvement is likely possible using UHV equipment. In the interphase of CrCxNy/Si samples, oxygen is incorporated to the detriment of carbon. The CrSixCy films analyzed by
SIMS were deposited on Ge#100. instead of Si#100. to avoid confusion on the origin of silicon. The silicon level in CrSixCy layers

Figure 7. RBSCrprofileofanas-depositedCr3#C,N#2filmgrownat400°ConaSiO2/Sisubstrate.
remains constant even in the ultrathin oxidized sublayer #Fig. 6b#.In this interphase, oxygen is incorporated to the detriment of carbon and chromium.

The EPMA analyses of as-deposited amorphous CrCxNy films give the average composition Cr0.53C0.34N0.13. Interestingly, this is in the existing range of the ternary compound Cr3#C0.8N0.2#2 #Table II#. The nitrogen content of our films is close to the upper limit previously reported for this ternary phase.34,44-46 These analyses reveal also a slight excess of carbon in the layers, which is probably
present in the form of free carbon #graphitic or amorphous#.

From EPMA data, the density of as-deposited CrCxNy films has been estimated to be 5.2. This is lower than the value of 6.5 reported for bulk Cr3#C,N#245 as generally observed for thin film materials. However, this is intermediate between the typical values reported for CVD TiN and TaN layers, 2.5-4.115 and 5.8-9.6,47,48 respectively.

RBS analyses #He+ ions, 2 MeV. of relatively thick CrCxNy films ##180 nm. show only a slight oxygen contamination, whereas for thinner films #30-40 nm. the oxygen content can reach 30 atom %. This is in agreement with SIMS profiles which have revealed the existence of a thin oxidized interphase for some of the samples. Obviously, for ultrathin films this interphase becomes dominant. In the thicker films, the depth distribution of the elements is uniform, as observed with the SIMS analyses, and the Cr content was found to be #60 atom % #Fig. 7#. Interestingly, this value is in very good agreement with that of the ternary compound Cr3#C0.8N0.2#2. From RBS analyses, a Cr atomic density of

7.3 . 1022 atom cm-3 was determined, which is very close to the value calculated from the structure of Cr3#C0.8N0.2#2 #11 . 1022 atom cm-3#.34

XPS analyses of CrSixCy layers show the presence of chromium, silicon, and carbon with an oxygen contamination which depends on the thickness of the films, in good agreement with SIMS analyses. No other impurity was detected. The binding energy of the Cr 2p3/2 level is characteristic of either a chromium carbide or silicide; the difference between the two types is below the resolution of our spectra. However, there is no evidence for a chromium oxide contribution. The C 1s peak shows at least two forms of carbon: a carbidic one at 283.0 eV and free carbon at 284.5 eV. The Si 2p peak at 102.0 eV is characteristic of SiOx. Thus, the oxygen is mainly bonded to silicon in agreement with the high affinity of Si for oxygen.

XPS and EDX quantitative analyses indicate a slight increase of the Cr/Si ratio with the deposition temperature #Table III#. This

Table III. Composition and electrical resistivity of as-deposited CrSixCy layers as a function of the deposition temperature. For composition analysis, the films were grown on Si(100) (except where otherwise specified), while SiO2/Si substrates were used for resistivity measurements.

Deposition temperature #°C.	Cr/Si atomic ratio EDX	EPMA	XPS	Resistivity ##. cm.
400	1.1	--7	.	107
450	1.3	--1.6	.	107
475	1.6	1.6a	2.1	105
500	1.8	-2.2		105

a Ge substrate, film thickness 480 nm.

probably corresponds to a decrease of Si content in the layers due to a better elimination of organosilicon groups from the surface to the gas phase when the temperature is increased. Because of the low thickness of the CrSixCy films and of their oxygen contamination, EPMA analysis was difficult. The most reliable EPMA data were obtained for a relatively thick film #480 nm. deposited on a Ge substrate at 475°C which gives a Cr/Si ratio of 1.6. This value is similar to that of Cr5Si3Cx#0.25 . x . 1.05#, Cr/Si = 1.67, which is the single ternary phase of the Cr-Si C system.49,50

Annealing treatment.— In order to test the thermal stability of the films deposited on Si and SiO2 substrates, and thus the behavior

of the film/substrate interfaces, they were annealed under different conditions and the structural variations were analyzed by XRD.

Annealing under vacuum.—CrCxNy samples were annealed under static vacuum ##10-3 Torr#. They were sealed under vacuum in quartz ampuls and heated in a furnace for variable durations.

The amorphous structure of CrCxNy films deposited at 380°C does not change significantly after annealing at 600°C for 60 min. After 120 min at the same temperature, three broad peaks located approximately at . = 19°, 22°, and 32° appear #Fig. 8a#. This reveals the beginning of a structural organization at the nanometric scale but there is no evidence for crystallization. It is noteworthy that these broad peaks correspond to those observed for as-deposited films grown at higher temperatures #430-450°C#. By contrast with the low-temperature layers, the films deposited at 430°C readily crystallize after the treatment at 600°C for 60 min and the ternary phase Cr3#C0.8N0.2#2 is clearly identified #Fig. 8b#. These films are single-phased since no other crystalline phase appears on the XRD diagrams. The crystalline films keep the mirrorlike surface morphology and their shiny metallic appearance.

It is well known in MOCVD processes that when the deposition temperature is sufficiently low, organic species originating from an incomplete decomposition of the metallorganic precursor can be incorporated in the growing layers. This can delay or block the crystallization of the film. We assume this occurs for the CrCxNy films deposited at 380°C. In the case of the films deposited at higher temperature #430°C#, the contamination by organic species is minimized and they can be released more easily from the film, which will induce the crystallization. The SIMS profiles recorded before and after vacuum annealing reveal a reduction of an order of magnitude of the hydrogen content in the film #Fig. 9#. This certainly supports the release of H2 or organic species during the crystallization of the films. Besides, the annealing does not change the distribution profiles of the main elements.

Keeping in mind that for barrier applications amorphous and thermally stable layers are required, it was interesting to study annealing conditions under which the CrCxNy films could be more stable. From this point of view, assuming the crystallization is strongly related to hydrogen release, the crystallization could be hindered whether the samples were heated under H2 atmosphere.

Figure 8. InfluenceoftheannealingtimeonthestructureofCrCxNy filmsgrownat#a#380°Cand#b#430°ConSi#100#substrates.Theannealingwasperformedat600°Cunder vacuum.

Annealing under H2 ambient.—CrCxNy samples were annealed under H2 atmosphere at different temperatures ranging from 550 to 700°C for 30 min. These experiments were carried out directly in the CVD reactor under H2 stream.

As shown in Fig. 10, the only change observed in the XRD patterns at 550 and 650°C is a splitting of the hump centered at 21°

into two broad peaks. This may correspond to a transformation from
an amorphous to a nanocrystalline structure. A major change is observed after annealing at 700°C since the film crystallizes to form
the orthorhombic phase Cr3#C0.8N0.2#2. Interestingly, the crystallization occurs at a temperature significantly higher than for the annealing under vacuum. Furthermore, there is no evidence for reactions at
the film/substrate interface during this treatment since, for instance,
chromium silicides were not observed. The crystallization of the
layers is a failure mode of diffusion barriers because the grain
boundaries constitute fast diffusion paths for copper. From this point
of view, the structural stability of as-deposited CrCxNy is fairly
good.

Taking into account the above results, the annealing of CrSixCy
films was not performed under vacuum. The films are XRD amorphous whatever their thickness and the nature of the substrates.
CrSixCy samples were annealed at 700°C from 1 to 15 h under H2
atmosphere and no change was observed on their XRD patterns, i.e.,
the films are still amorphous #Fig. 11#. This reveals an excellent

Figure 9. SIMSdepthprofilesofaCrCxNy filmgrownat430°ConSi#100#:
#a#as-deposited;#b#afterannealingundervacuumat600°Cfor60min.
thermal stability of these CrSixCy films. By increasing the temperature, the amorphous structure starts to change after several hours at
850°C. For instance, after 6 h at 850°C under H2 ambience, several
broad peaks appear revealing the formation of one or several nanocrystalline phases resulting from either the crystallization of the film
or the reaction at the interface with the substrate #Fig. 11#. The
identification of the phases was unsuccessful due to the low intensity
and the width of the peaks, and to the fact that they appear in the
range where most of the possible phases have their principal peaks.
However, the most probable assumptions would be the crystallization of a carbide like Cr7C3, or a silicide #Cr3Si#, or possibly the
ternary compound Cr5Si3Cx, or a mixture of these three phases,
which are known to be thermodynamically stable at high

temperature.

Resistivity.— The electrical resistivity of preliminary CrCxNy
films tended to increase by decreasing the film thickness and a scattering of the measurements was observed for the thinner films. This
was due to the presence of the oxidized interphase which played a
dominant role in the thinner films. After an improvement of the
process in the early stages of the growth, especially after in situ
analyses by IR pyrometry,42 this was overcome and the resistivity
was typically lower than 1000 #. cm even for thicknesses of
25 nm.

In the narrow temperature range 400-450°C, no effect of the

deposition temperature was found on the resistivity of CrCxNy films.
Furthermore, no increase of resistivity was observed for CrCxNy

Figure 10.
Grazingincidence#2°#XRDpatternsofCrCxNy#190nm#/SiO2/Sisamplesafterannealingatvarioustemperaturefor30minunderH2atmosphere.Thegroupofpeaksaround27-28°originatesfromthesubstrate.
films after storage for several months in the laboratory atmosphere.
This is probably due to the good density of these layers that do not
take ambient oxygen.

The resistivity of as-deposited CrCxNy films grown at 420°C on
SiO2/Si substrates is typically 550 #. cm and is not affected by
annealing under H2 atmosphere until 650°C. Above this temperature, the resistivity decreases suddenly to 150 #. cm because
of the crystallization of the films #Fig. 12a#. The resistivity
of CrCxNy films annealed at 550°C, which is just below the crystallization temperature, increases slightly after 30 min from
550 to 600 #. cm, then remains stable for at least 6 h. This reveals
a good behavior of this thin film material at this temperature #Fig.
12b#. The slight increase of the resistivity during the early stages of
this annealing treatment is likely due to the transition of the quasiamorphous structure of as-deposited films to the nanocrystalline
structure #Fig. 10#.

The resistivity of as-deposited CrSixCy films decreases almost
three orders of magnitude by increasing the deposition temperature

Figure 11. Grazingincidence#2°#XRDpatternsofCrSixCy
layersafterannealingunderH2atmosphereforvarioustimesandtemperatures.Thegroupofpeaksaround27-28°originatesfromthesubstrate.

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Figure 12.
InfluenceoftheannealingconditionsunderH2atmosphereontheresistivityofCr3#C,N#2#190nm#/SiO2/Sisamples:#a#effectoftheanneal-
ingtemperature#time=30min#;#b#effectoftheannealingtimeat550°C.

from 400 to 500°C to reach 105 #. cm at 475°C #Table III#. This value is higher than the literature data reported for conducting diffusion barriers #TiN, TaN,…#28 or even for CrCxNy layers. Values as high as 105 #. cm were reported for layers in the Cr-Si-O system,51 whose microstructure was heterogeneous and consisted of metal particles embedded in an insulating matrix. According to these authors, the insulating matrix was SiO2, and the conducting or semiconducting particles were chromium or chromium silicide. In our case, the undesirable incorporation of oxygen in the CrSixCy layers, confirmed by XPS, EPMA, and SIMS analyses, may explain to some extent their high resistivity. According to XPS data, oxygen is preferentially bonded to silicon rather than chromium. However, there is no clear evidence for a heterogeneous structure of our CrSixCy films, beside the presence of a fine oxidized interphase. Nevertheless, oxygen is present in the entire thickness of the layers likely at a sufficient level to affect the resistivity. Plasma posttreatment of TiN thin films was reported as a promising method to reduce the oxygen contamination of barriers grown using metallorganic precursors.52,53 The influence of such post-treatments has to be investigated on these MOCVD Cr-based layers.

Conclusions

Two types of Cr-containing thin films were deposited under low pressure by MOCVD on Si#100. and SiO2/Si substrates in the temperature range 380-450°C for CrCxNy and 450-500°C for CrSixCy.
The molecular compounds Cr#NEt2#4 and Cr#CH2SiMe3#4 were used as a single-source precursor, respectively. The growth was

achieved in a cold-wall reactor using, respectively, H2 and He as carrier gas. Both types of films exhibit a mirrorlike surface morphology with a shiny metallic appearance.

As-deposited CrCxNy layers are amorphous or nanocrystalline depending on the deposition temperature. They start to crystallize at 600°C after annealing for 1 h under vacuum, whereas the crystallization occurs at 650°C during a heat-treatment under H2 atmosphere. In both cases, the original ternary phase Cr3#C0.8N0.2#2 is formed. The resistivity of as-deposited amorphous CrCxNy films is typically 550 #. cm and was found to decrease to 150 #. cm for polycrystalline films Cr3#C,N#2 after annealing.

As-deposited CrSixCy films are amorphous and they exhibit an excellent thermal stability since no structural features appear after annealing at 700°C for 15 h or at 850°C for 4 h. Under more severe conditions, a mixture of various phases starts to crystallize including

possibly Cr7C3,Cr3Si, Cr5Si3Cx, and the like. The CrSixCy films exhibit a high resistivity due in part to an oxygen contamination of these films.

These Cr-based layers exhibit properties which make them interesting for applications as diffusion barriers in copper metallization.
Their performances against the diffusion of copper will be evaluated in a companion paper.39

Acknowledgments

The authors gratefully acknowledge Dr. H. Vergnes and Dr. F. Dupuy, Toulouse, for the hydrodynamic simulation, Dr. O. Demolliens, LETI, Grenoble, for supplying us with substrates, and R. Madar, Grenoble, for fruitful discussions.

Centre Interuniversitaire de Recherche d'Ingéniere des Matériaux assisted in meeting the publication costs of this article.

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