ION BEAM ANALYSIS OF TERNARY SILICIDES Me-Si-N (Me = Re, Ta, Ti, W) THIN FILMS USED AS DIFFUSION BARRIERS IN ADVANCED METALLIZATION

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Copper is the most widely accepted material for advanced metallization especially as interconnects for future semiconductor devices. However, copper is a fast diffuser in silicon and other materials of integrated circuits during thermal treatments. Highly effective diffusion barriers are thus essential if copper has to become the future interconnects metal. LPCVD ternary silicides Me-Si-N (Me = Ta, Ti, W, Re) are investigated for such applications. To optimize the deposition process, accurate characterizations of the elements constituting the material are needed. Quantitative profiles of the elements have been measured using ion beam analysis. An original method for nitrogen profiling based on nuclear reaction spectroscopy has been developed. Films stoichiometries and their evolution with device annealing have been obtained.

INTRODUCTION

The decreasing dimensions of electronic devices clearly intensify the need for the introduction of new materials in the advanced VLSI and ULSI (Very and Ultra Large Scale Integrated) technologies. For instance, aluminum is the metal of choice for metallization in silicon integrated circuits in LSI (Large Scale Integration) thanks to its low contact resistance and ease of processing. But in sub-micron geometries, aluminum has to be replaced because of junction spiking and electromigration. Copper becomes the most widely accepted material for advanced metallization since it presents a lower resistivity and higher electromigration resistance (1). However, copper is a fast diffuser in silicon and other materials of integrated circuits during thermal treatments (2), highly effective diffusion barriers have to be interposed between them (3). Since the beginning of the 1990’s, a novel material field has been explored (4). Ternary amorphous metallic thin films such as TaSiN (5), TiSiN (6), WBN (7), WSiN (8) composed of a transition metal, one non metal component (Si or B) and nitrogen have been developed. Most of them are fabricated by Physical Vapor Deposition (PVD) with a structure which appeared to be amorphous by XRD analysis. With crystallization temperatures that approach the 1000°C range, they are considered
as viable candidates for diffusion barriers. An attractive alternative way to produce these materials is a Low Pressure Chemical Vapor Deposition process, especially because of its ability to provide good step coverage. LPCVD ternary silicides Me-Si-N where Me = Ta, Ti, W and Re have been deposited on SiO₂/Si and silicon substrates, starting from silane, in situ fabricated metal chlorides, ammonia, hydrogen and argon. The experimental deposition processes and the combined thermodynamic approaches have been thoroughly presented elsewhere (9,10). The films are characterized by X-Ray Diffraction, Scanning and Transmission Electronic microscopies, electrical resistivity. MeSiN layers deposited on patterned substrates show a very good step coverage which demonstrates the potentialities of the given CVD process. Performances of the four copper metallized MeSiN systems, tested by Auger depth profiles appear to be strongly dependent on the film composition. Therefore, to optimize the procedure, accurate characterizations of the elements constituting the material are needed. This study deals with the different techniques using ion beam analysis that may be carried out to analyze light elements, such as nitrogen.

EXPERIMENTAL PROCEDURE

Different techniques using ion beam analysis such as Rutherford Backscattering Spectrometry (RBS), Nuclear Backscattering Spectrometry (NBS) and Nuclear Reaction Spectroscopy (NRS) are investigated to obtain the elements distribution profiles in the Me-Si-N films. The Rutherford Backscattering Spectrometry (RBS) technique provides the profiles of heavy elements (Ti, Ta, W and Re) using incident energies around 2 MeV. However, it cannot be utilized for a global analysis because of its lack of sensitivity to separate and profile the light elements, like nitrogen and oxygen. Nuclear backscattering spectrometry NBS differs from RBS by the fact that the outgoing elastic channel which is made possible by the low coulomb barrier on light elements. For alpha incident energies higher than 3 MeV, NBS allows to profile light elements such as carbon, oxygen and nitrogen. In the present study, it is difficult to take advantage of the high NBS cross sections observed on C, N, O for alpha incident energy higher than 5 MeV, since the non Rutherford cross section of silicon Si(α,α) (11) presents several resonances which interfere with those of the other measured elements. Finally, the adopted solution is the analysis by elastic diffusion with an incident energy of 3.53 MeV. In this energy domain, the diffusion cross section of oxygen is Rutherford (σ/σ₀=1), whereas the nitrogen one is resonant (σ/σ₀=2.3). Moreover, this energy domain corresponds to a smooth variation of the Si(α,α) reaction cross sections, consequently the light elements response superimpose on a monotonous background. The analysis that are carried out at this energy give the distribution profiles of the refractory metals, the heavy impurities (Cl), silicon and the interfacial oxygen. Nevertheless, a more selective method is necessary to profile nitrogen. The Nuclear Reaction Spectroscopy -NRS- technique using the ^1^4N(α,p)^1^7O reaction is investigated. Several reactions have been already utilized (12-14) for the
nitrogen analysis. The cross section has been measured by Herring (15) and Kashy (16) in 1958 and more recently by Lin and col. (17).

The reaction mechanism can be written as:

\[ ^{14}N + ^{4}\alpha \rightarrow ^{18}F* \rightarrow ^{1}p + ^{17}O \]

To separate the contributions \((\alpha,\alpha)\) and \((\alpha,p)\), the protons and the \(\alpha\) particles have to be separated. The most appropriate identification method consists in using a two detectors telescope. The first one labeled \(\Delta E\), which is a thin detector (19 \(\mu m\)) connected in transmission mode, measures the energy loss of the particle. The second one, labeled \(E\), measures its residual energy. A classical spectrometry line is associated to each detector. The total particles energy \(E_t\) is obtained by the sum of \(\Delta E\) and \(E\) signals.

Particle identification is done by feeding the \(\Delta E\) detector data, event by event, into computer along with the \(E\) data. Figure 1 shows a biparametric experimental spectrum obtained on 2.6 \(\mu m\) thick NbTiN standard with an \(\alpha\) incident energy of 5.9 MeV, and a detection angle of 172 degree. The proton emitted in the \(^{14}N(\alpha,p)^{17}O\) reaction are clearly identified.

![Biparametric spectrum](image)

Figure 1. Biparametric spectrum of a 2.6 \(\mu m\) thick NbTiN standard.

The projection of the proton energy distribution on the total energy axis is given on figure 2. The analysis will be focus on the \(^{14}N(\alpha,p)\) component.
Figure 2. Emitted protons in the $^{14}$N($\alpha$,$p$)$^1$O reaction

Because of $^{28}$Si($\alpha$,$p$)$^{32}$p reaction which occurs on the silicon substrate on top of which the Me-Si-N are deposited, a kinematic study is needed in order to avoid overlap of proton spectra emitted respectively in the $^{14}$N($\alpha$,$p$) and $^{28}$Si($\alpha$,$p$) reactions. The optimal conditions correspond to an incident energy of 3.8 Mev and a detection angle of 160 degree. In such conditions only protons emitted in the $^{14}$N($\alpha$,$p$) reaction have enough energy to be identified. Moreover, the value of 3.8 MeV for the analysis energy corresponds to a resonance of the reaction $^{14}$N($\alpha$,$p$) which is frequently adopted for the nitrogen measurement (17,12).

**CHARACTERIZATION OF THE Me-Si-N TERNARY SYSTEMS**

The four systems Me-Si-N where Me= Re, W, Ti, Ta have been investigated as a function of the refractory metal. Ternary MeSiN films are fabricated in a vertical cold wall low pressure reactor, starting from in situ produced gaseous metal chlorides, silane, ammonia and hydrogen. The optimal deposition conditions in terms of appropriate films properties for diffusion barrier applications and/or minimal deposition temperature are given on table 1 (9).

<table>
<thead>
<tr>
<th></th>
<th>Deposition T ($^\circ$C)</th>
<th>Chlorination T ($^\circ$C)</th>
<th>Total pressure (Pa)</th>
<th>Cl\textsubscript{2} flow rate (sccm)</th>
</tr>
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<tbody>
<tr>
<td>ReSiN</td>
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<td>550</td>
<td>1197</td>
<td>5</td>
</tr>
<tr>
<td>WSiN</td>
<td>500</td>
<td>800</td>
<td>665</td>
<td>4</td>
</tr>
<tr>
<td>TiSiN</td>
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<td>750</td>
<td>1330</td>
<td>2.5</td>
</tr>
<tr>
<td>TaSiN</td>
<td>650</td>
<td>650</td>
<td>1330</td>
<td>5</td>
</tr>
</tbody>
</table>
a- Results in ReSiN system

Preliminary analysis of the quantitative elementary profiles deduced from ion beam techniques shows that for a given ratio silane/ammonia flow rates of 166 (SiH$_4$ = 500 sccm and NH$_3$ = 3 sccm), the produced films are essentially composed from Re and Si, with a low content in nitrogen (3% massic, 10 at %). The nitrogen element has diffused in the interface and the substrate. With a SiH$_4$/NH$_3$ ratio close to 66, the film thickness depends on the active gases flowrates. The figure 3 shows the elements profiles for a film obtained with a SiH$_4$/NH$_3$ ratio equal to 65 (SiH$_4$ = 650 sccm and NH$_3$ = 10 sccm). It appears that a ReSiN mixture film has been formed with a 250 μg/cm$^2$ thickness. There is no nitrogen diffusion in the substrate. The nitrogen quantity (10 % massic, 42 at %) is constant along the film depth. In the same way, the rhenium element profile is homogeneous along the film depth (73 % massic, 24 at %), but there is some rhenium diffusion in the interface and in the silicon substrate.

![Figure 3. Distribution profiles of the ReSiN elements along the film depth.](image)

The analysis gives an average composition of Re$_{0.24}$Si$_{0.31}$N$_{0.42}$ on the 250 μg/cm$^2$ thickness (thickness = 400 nm). The chlorine contamination is around 3 at % all along the film depth. In the ternary phase diagram, the ReSiN average composition is located in the stability domain close to the Re + Si$_3$N$_4$ equilibrium tie-line, corresponding to a mixture of about 1/4 Re + 3/4 Si$_3$N$_4$ (10). These results have been confirmed by X-Ray Diffraction which indicates that the as deposited films present a nanocrystalline or amorphous morphology and crystallise in Re after annealing, and by Transmission Electronic Microscopy which shows that the ternary alloy appears as a composite of very small particles identified as Re inserted in a non-crystallized "Si$_3$N$_4"$ matrix. In the case of the same SiH$_4$/NH$_3$ ratio close to 66, with silane and ammonia flow rates of 200 and 3 sccm, respectively, the film thickness does not exceed 10 mg/cm$^2$ and nitrogen and rhenium diffusion in the interface are observed.
b- Results in WSiN system

A similar methodology has been followed for the WSiN system. The film thickness is around 185 μg/cm². Chlorine contamination is found to be 8 at % and oxygen is present at the interface. An average composition of W₉₂₅Si₃₂₅N₈₂₅ is calculated. X-Ray diffraction and TEM evidence the coexistence of tungsten nanograins and an instable phase W₂N in a non-crystallized "Si₃N₄" matrix (10). In order to evaluate the thermal stability of the films, as deposited and annealed (under vacuum at 900°C) films have been examined, results are shown on figure 4 and 5.

Ion beam analysis indicates that after annealing:

1- there is a tungsten accumulation at the surface, which is shown on figure 4 where the tungsten distribution profiles before and after film annealing are plotted. This can be related to a nitrogen out-gazing and decomposition of the W₂N phase which have been evidenced with X-Ray Diffraction, SEM and TEM observations.

![Figure 4. Tungsten distribution profiles obtained by RBS on as deposited and annealed sample.](image)

2- The nitrogen content decrease is also revealed with the NRS response. Comparison of biparametric spectra (figure 5a and 5b) put into evidence the nearly total vanishing of the ¹⁴N(α,p) contribution, which means that nitrogen concentration in the annealed sample is lower than the detection sensitivity.
c- Results in TiSiN and TaSiN systems

Whatever tested deposition conditions, TiSiN and TaSiN films have been obtained with a crystallised morphology, which is not appropriate for the investigated application. The crystallised phases are found to be the metal nitrides TiN and TaN. Moreover, the ion beam analysis shows that the silicon content is very low (below 10 at % and close to 0 for TiSiN and TaSiN, respectively). The deposited films are essentially composed from the metal nitrides, which can be explained by their high stability.
CONCLUSION

The tested ion beam analysis methods have been used to determine the distribution profiles of the elements constituting the LPCVD MeSiN films and, consequently, the film composition. This method has been found to be really useful and complementary for the film characterization and finally the process optimization, associated with the other characterization techniques such as X-Ray Diffraction, Transmission and Scanning Electronic microscopies, and the corresponding ternary phase diagrams. The major interest consists in an accurate evaluation of the light elements contents. Particularly, it provides the evolution of the nitrogen content with the film annealing.

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REFERENCES