

## HIGHLY CONFORMAL DIFFUSION BARRIERS OF AMORPHOUS NIOBIUM NITRIDE

R. G. GORDON\*, X. LIU\*, R. N. R. BROOMHALL-DILLARD\* AND Y. SHI\*\*

\*Harvard University Chemical Laboratories, 12 Oxford Street, Cambridge, MA 02138

\*\*Chemat Technology, Inc., 19365 Business Center Drive, Northridge, CA 91324

### ABSTRACT

Electrically conductive films of niobium nitride were formed by chemical vapor deposition from tetrakis(diethylamido)niobium and ammonia. The films were found to be highly conformal, with step coverage nearly 100% for substrate temperatures near 350 °C. The structure of the films was amorphous by diffraction of X-rays and electrons. The reliability of the films as barriers to diffusion of copper was also tested.

### INTRODUCTION

In computer processors and memory chips, metal circuits connect transistors and capacitors formed near the surface of the silicon. Aluminum and tungsten are the metals commonly used for the circuit interconnections. Copper is starting to be used in place of these metals because of its lower electrical resistance and better durability against electro-migration. In order to provide a functional and durable computer, these metals must be separated from the silicon and the interlayer dielectrics by barrier/adhesion layers. In the absence of such barrier/adhesion layers, aluminum could alloy with the silicon, producing etch pits that can short out the electrical circuits; tungsten could peel off of the silicon dioxide insulating layers; copper could diffuse into the silicon and provide deleterious recombination centers for the electrons and holes; and copper could corrode or delaminate.

Titanium nitride is the material that is usually used as the barrier layer. The titanium nitride is ordinarily formed by the process of reactive sputtering of a titanium target in a low pressure of nitrogen gas. The sputtered material has been satisfactory for the production of computer chips with feature sizes down to about one-quarter of a micron. As the industry tries to make the circuits operate faster and store more information, the feature sizes are being reduced. For feature sizes less than about one-quarter of a micron, sputtering does not cover adequately the sides and bottoms of the narrow holes and trenches that are etched a micron deep into the substrates.

The coverage of the side walls and bottoms of the etched features must have a film thickness on the same order as the outer surface. This relationship is described as "step coverage." Step coverage is defined as the ratio of the thickness of the deposited film at the bottom of the holes to the thickness of the film on the top of the silicon dioxide layer. The barrier layer must have step coverage close to one. Thus a need is perceived for barrier layers deposited by a process that has better step coverage than sputtering can provide.

Good step coverage is provided by thermal chemical vapor deposition<sup>1</sup> (CVD) of tetrakis(dimethylamido)titanium (without added ammonia).<sup>2</sup> The good step coverage is attributed to the low sticking coefficient of the titanium amido compound and any reaction intermediates produced by it. Molecules with low sticking coefficients can survive numerous

collisions with the side walls of a hole without depositing material. Hence, the molecules are more likely to deposit further within the hole and to give good step coverage. Unfortunately, the observed good step coverage for this process is accompanied by high carbon contamination of the films, high electrical resistivity, and porosity (low density).

Better quality titanium nitride films have been obtained by a CVD process for the deposition of titanium nitride from vapors of tetrakis(diethylamido)titanium and ammonia.<sup>3</sup> This process operates at substrate temperatures below 400 °C, which are low enough for use in semiconductor microcircuits. The step coverage obtained by this process is adequate for forming barrier layers on microcircuits currently produced with feature sizes around one-quarter of a micron and aspect ratios at least up to 4:1. The step coverage can be improved by adding trimethylamine to the CVD gas mixture.<sup>4</sup>

Another potential problem for the use of titanium nitride in future generations of computer chips is that thinner layers may not be effective diffusion barriers. For features below 0.25 micron, very thin diffusion barriers will be needed so that the barrier material does not take up too much of the space needed for the copper.<sup>5</sup> Titanium nitride films have a microcrystalline structure. Diffusion of copper through thin titanium nitride barriers might occur along boundaries between the microcrystalline grains. This leakage might be prevented by “stuffing” the grain boundaries with impurities such as oxygen.

Amorphous diffusion barriers are expected to perform better than microcrystalline ones because amorphous materials lack intergranular pathways for diffusion. Titanium nitride films can be made amorphous by addition of silicon, but the resistivity increases greatly.<sup>6</sup> Amorphous tantalum nitride<sup>7</sup> or niobium nitride<sup>8</sup> form the most conductive thin barriers to diffusion of copper that are known. Unfortunately, the sputtering processes commonly used to make amorphous tantalum nitride or niobium nitride do not provide adequate step coverage. Somewhat better step coverage is currently obtained with ionized PVD, but this process may not be successful for future smaller design rules.

CVD processes, which might produce better step coverage, were previously reported for niobium nitride<sup>9</sup> and tantalum nitride<sup>10</sup> at deposition temperatures above 500 °C, which is too high for most microelectronic applications.

#### Low-Temperature CVD Process for Amorphous Niobium Nitride Barriers

This CVD process<sup>11</sup> involves the reaction of ammonia gas with the vapors of niobium dialkylamide compounds such as niobium(V) dimethylamide, Nb(NMe<sub>2</sub>)<sub>5</sub>, or niobium(IV) diethylamide, Nb(NEt<sub>2</sub>)<sub>4</sub>. The typical substrate temperatures are below 350 °C, and thus are compatible with silicon semiconductor processing. The carbon content of the deposited films is low (<1 atomic %), generally below the detectability limit of X-ray photoelectron spectroscopy (XPS) or Rutherford backscattering spectroscopy (RBS). The electrical resistivities of these niobium nitride films were around 1000 μΩ-cm. Further optimization of this process may produce resistivities low enough (below about 250 μΩ-cm) for applications as a thin conducting barrier in microelectronics.

The analogous low-temperature CVD reactions for tantalum nitride<sup>11</sup> produce an electrically insulating form of tantalum nitride, Ta<sub>3</sub>N<sub>5</sub>, which is not suitable for electrically conductive barrier applications. In contrast, all known niobium nitride phases are electrically conductive, and an analogous insulating Nb<sub>3</sub>N<sub>5</sub> phase is not known and is probably unstable. This is one of

the few differences between these elements, niobium and tantalum, which are otherwise almost identical in their properties. Thus this paper focuses on thermodynamically stable and conducting niobium nitride, rather than the more thoroughly studied tantalum nitride which can form its thermodynamically stable insulating nitride phase.

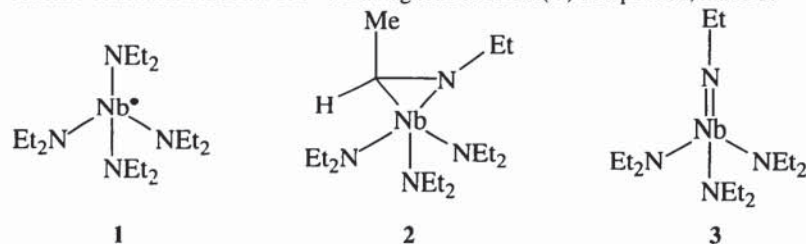
Of the two chemical precursors used for CVD of niobium nitride, niobium(V) dimethylamide,  $\text{Nb}(\text{NMe}_2)_5$ , is a solid, and niobium(IV) diethylamide,  $\text{Nb}(\text{NEt}_2)_4$ , is a liquid.<sup>12</sup> In practical applications of CVD to industrial manufacturing processes, liquid sources are always preferred to solids. Liquids are more easily handled and transferred, and can be pumped and vaporized at very well-controlled and high rates. Solids, on the other hand, require labor-intensive efforts to transfer between containers, cannot be pumped or metered continuously and quantitatively, and vaporize at slow and non-reproducible rates. For these reasons, this paper will focus on liquid niobium(IV) diethylamide as a CVD precursor.

## EXPERIMENT

Bradley and Thomas<sup>12</sup> reported the original synthesis of “niobium(IV) diethylamide” by the reaction of niobium(V) chloride with lithium diethylamide:



followed by distillation of the crude reaction products. The “ $\text{Nb}(\text{NEt}_2)_4$ ” prepared in this way was later found to be a mixture rather than a pure compound.<sup>11</sup> We have now determined by NMR analysis that this mixture consists of three compounds. Only about 17% per cent is actually the paramagnetic niobium(IV) diethylamide,  $\text{Nb}(\text{NEt}_2)_4$ , (compound **1**), while the majority consists of similar amounts of two diamagnetic niobium(V) compounds, **2** and **3**:



Heating this liquid mixture at 140 °C for 2 days converted the mixture almost entirely (>99%) to compound **3**, ethylimido-tris(diethylamido)niobium(V). Experiments were conducted with both the crude precursor mixture and with pure **3**, with equivalent results. Presumably, when the vapor mixture is heated in the CVD reactor, it also converts to **3**. Imide formation is a dominant decomposition pathway for analogous tantalum compounds.<sup>13</sup>

The precursors were loaded into a gas-tight syringe in an inert atmosphere glove box. The syringe was then placed in a syringe pump. The viscosity of the precursor mixture was measured to be 7.3 centipoise (cp). This value is low enough so that it could be nebulized with a Sonotek ultrasonic spray nozzle operating at 125 kHz, producing droplets around 30-50 μm in diameter. The resulting fog was then mixed with a flow of preheated nitrogen in order to vaporize it

quickly. In some experiments, the nitrogen was not preheated, so the evaporation took place within the heated tube furnace. Ammonia diluted with nitrogen was introduced separately into the tube furnace in order to avoid premature reaction.

Some experiments were carried out with a Cetac ultrasonic nebulizer operating at 1.44 MHz, producing still smaller droplets (diameters 10-20  $\mu\text{m}$ ). The Cetac nebulizer works best with lower viscosity liquids. Thus for this system, the precursor was diluted with three times its volume of mesitylene, which has a combination of low viscosity (0.6 cp) and low vapor pressure, so that it does not evaporate too soon.

Measurements of growth rate, composition, electrical resistivity, step coverage, and barrier properties were carried out. The compositions of the films were determined by Rutherford Backscattering Spectroscopy (RBS), by Forward Recoil Spectroscopy (FRS), and by X-ray photoelectron spectroscopy (XPS), and thicknesses by X-ray reflectometry.

## RESULTS

The films were composed niobium, nitrogen, hydrogen, and oxygen. No carbon signal (expected near 284 eV) was detected (<1 at. %), as shown by the XPS spectrum in Figure 1. (The unmarked peaks are also due to niobium.)

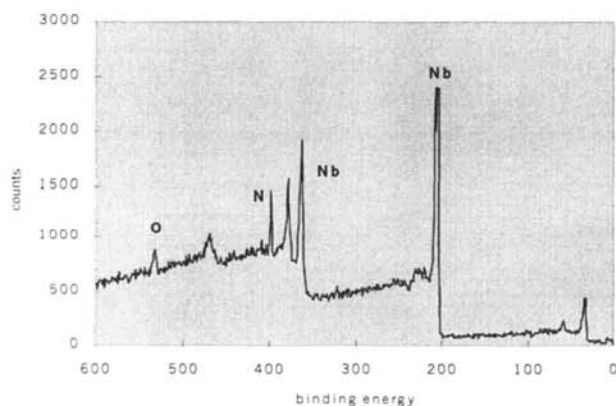


Figure 1. X-ray photoelectron spectrum of a niobium nitride film after cleaning by sputtering.

The nitrogen to niobium ratio was found to be about 1.3 by RBS, corresponding to a niobium(IV) nitride phase  $\text{Nb}_3\text{N}_4$ . Hydrogen was detected by FRS at parts-per-million levels in the films. Varying amounts of oxygen were detected, arising from traces of oxygen or water vapor in the deposition region. A major source of oxygen contamination was from water desorbing from the Pyrex glass tube. Most of this water could be blocked by precoating the inside of the tube with niobium nitride; the material deposited in a new glass tube always had much higher oxygen levels than subsequent depositions in the coated tube.

Neither X-ray diffraction nor electron diffraction detected any sharp lines. Thus the structure of the films is amorphous. Any undetected microcrystallites would need to be smaller than about 2 nm to escape detection. Growth rates varied along the length of the sample, because the precursor is depleted as it flows along the tube. The growth rate had a maximum of about 80 nm/minute near the entrance to the tube. The electrical resistivity was as low as about  $1000 \mu\Omega\text{-cm}$ . It was higher for films with higher amounts of oxygen, so when films are prepared without oxygen contamination, the resistivity is expected to be lower.

The cross-sectional micrographs in Figure 2 shows the high conformality and smooth surfaces of the niobium nitride films. The step coverage is 100% at substrate temperatures of  $320^\circ\text{C}$  or below and decreases at higher temperatures.

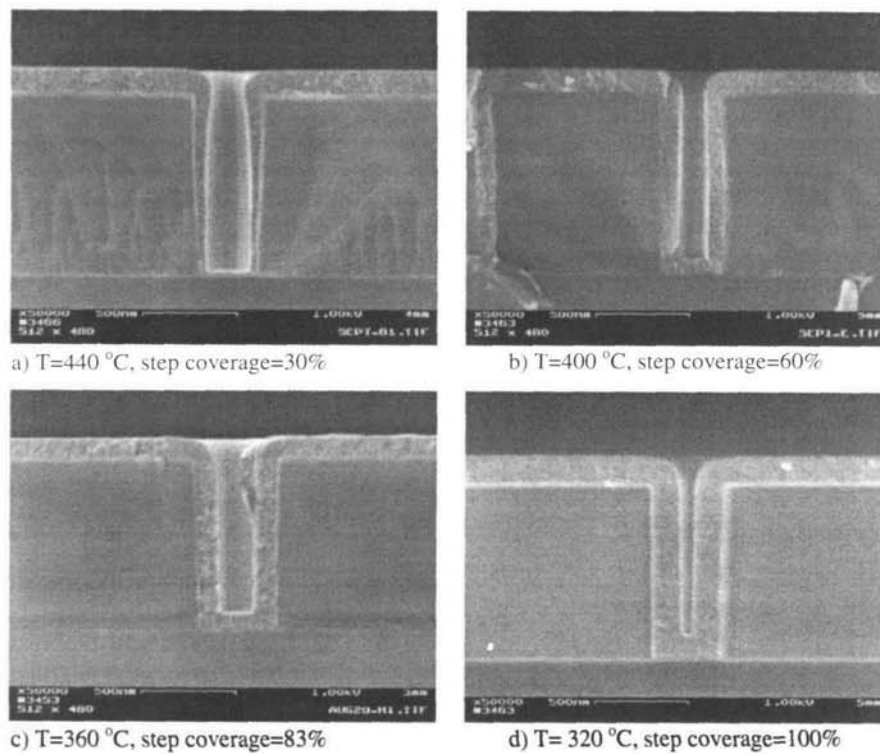


Figure 2. Cross section of a CVD amorphous niobium nitride film in holes with aspect ratio 3.5, deposited at substrate temperatures from  $320^\circ\text{C}$  to  $440^\circ\text{C}$

The effectiveness of the films as barriers to the diffusion of copper was tested. Special test wafers with lithographically defined transistors<sup>14</sup> were coated with niobium nitride. Then the wafers were further patterned, provided with electrical connections, and heated (to around  $200^\circ\text{C}$ ) under electrical bias to sense the effects of copper on the transistor behavior. Very thin

niobium nitride barriers (5 nm thick) lasted a maximum of 1 hour in this test. These times are likely to be shortened and scattered because of the presence of pinholes in the barriers, which were deposited in an ordinary laboratory. Better results are expected when these barriers are made and tested in clean-room conditions.

We conclude that CVD niobium nitride warrants further development and testing as a barrier/adhesion layer in microelectronics.

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