

## ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION OF TITANIUM NITRIDE FROM TITANIUM BROMIDE AND AMMONIA

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### ABSTRACT

Titanium nitride films were formed by chemical vapor deposition from titanium tetrabromide and ammonia at atmospheric pressure and substrate temperatures from about 400 to 600 °C. Although titanium tetrabromide is a highly hygroscopic solid at room temperature, it can be handled conveniently as a very concentrated liquid solution (85 weight per cent) in bromine as a solvent. This solution can be vaporized by a direct liquid injection system. Alternatively, the solution can be pumped into a bubbler, from which the bromine solvent is then removed by fractional distillation. Rutherford Backscattering Spectroscopy was used to determine that the bromine content of TiN deposited at 500 °C was about one atomic per cent. Growth rates were about 17 nm/min, and electrical resistivity was found to be about 200  $\mu\Omega$ -cm.

### PROPERTIES AND USES OF TITANIUM NITRIDE

Titanium nitride, TiN, is a hard, chemically inert electrical conductor with a high melting point. Its applications include wear-resistant coatings on machine tools, solar control on windows, and computer chips. In the microelectronics industry, sputtered TiN serves as a diffusion barrier between silicon and metals, and as an adhesion layer between silicon dioxide and tungsten. The step coverage provided by sputtered TiN is inadequate to provide good barrier properties in sub-micron vias. Chemical vapor deposition processes can provide improved step coverage, and thus in recent years there has been considerable interest in CVD TiN for applications in microelectronics.

In this paper, we will first review the features that are desired in a CVD process. Then we will survey the CVD reactions that have been reported to produce TiN, and rate their features with respect to the ideal. Then we will report the operating conditions and properties obtained by the CVD reaction of titanium tetrabromide and ammonia. Finally, we briefly compare the features of this reaction with those of other CVD reactions for TiN.

## DESIRABLE FEATURES OF A CVD PROCESS

An ideal CVD reaction should satisfy many requirements.

### Properties of the precursors:

- The precursors should be fluids (gases or liquids), not solids, at room temperature, in order to facilitate handling and metering.
- The precursors should be inexpensive to manufacture and to purify.
- They should remain stable during storage, and not react with air.
- They should be non-flammable, non-toxic, and non-corrosive.

### Vaporization of the precursors:

- Their vapor pressure should be sufficiently high (e.g., 1 Torr) at a relatively low temperature (e. g., less than 200 °C).
- They should be thermally stable at their vaporization temperature.
- They should vaporize rapidly and reproducibly, which is usually the case if it is a non-associated liquid (not a solid) at its vaporization temperature.

### CVD reaction:

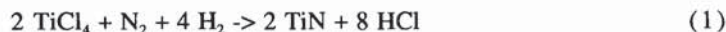
- The reaction should take place at a temperature low enough not to damage substrates.
- The reaction should produce a pure film, with high conductivity and good step coverage.
- A high percentage of the precursor should be converted to film.

### Byproducts:

- The byproducts of its CVD reaction should be stable and non-reactive.
- The reaction byproducts should be non-flammable, non-toxic and non-corrosive.

## SURVEY OF CVD REACTIONS USED FOR TiN BARRIERS

Several different CVD reactions have been used to deposit titanium nitride. The most commonly used precursor is titanium tetrachloride,  $\text{TiCl}_4$ . When reacted with molecular nitrogen, according to Eq. (1),



titanium nitride is deposited at appreciable rates only for temperatures over about 900 °C.<sup>1</sup> Although this process has been used commercially on refractory substrates such as tungsten carbide, the deposition temperatures are far too high for use in silicon-based microelectronics. The deposition temperature is reduced to about 500 to 700 °C by the use of ammonia as a nitrogen source in place of the molecular nitrogen.<sup>2</sup>



Preheating the reactant gases to around 250 °C is necessary in order to avoid adduct formation. Films deposited by reaction (2) contain significant amounts of chlorine (over  $2 \times 10^{21} \text{ cm}^{-3}$ ) if the reaction is carried out at temperatures below about 600 °C.<sup>3</sup> This chlorine causes corrosion of adjacent layers of aluminum, if the chlorine content exceeds about  $3 \times 10^{21} \text{ cm}^{-3}$  (about 3 atomic per cent); thus corrosion-resistant TiN layers can only be achieved by reaction (2) at substrate temperatures over about 600 °C.<sup>4</sup> The chlorine content may be reduced by the use of methylhydrazine as a nitrogen source in place of the ammonia.<sup>4, 5</sup> However, methylhydrazine is an extremely potent carcinogen (TLV < 10 ppb), and thus is unlikely to be accepted in production.

The chlorine can be eliminated altogether by using a metal-organic source, such as tetrakis(dimethylamido)titanium (TDMAT). Use of TDMAT alone, however, results in a film with high resistance and high carbon contamination.<sup>6</sup> Addition of ammonia to the TDMAT eliminates the carbon,<sup>7</sup> but degrades the step coverage. Using tetrakis(diethylamido)-titanium (TDEAT) along with ammonia produces pure, low-carbon films having moderately good step coverage and electrical resistivity adequate for applications in microelectronics.<sup>8</sup>

Use of titanium tetraiodide and ammonia in a LPCVD system has been reported to yield films with less than 1% iodine contamination even when the films were deposited at temperatures as low as 400 °C.<sup>9</sup> Unfortunately, titanium tetraiodide is a solid at room temperature (melting point 150 °C), so its delivery into a CVD system is not very convenient.

The advantages and disadvantages of these CVD reactions are summarized in Table I. Clearly none of the previously-reported reactions is fully satisfactory in all aspects.

Table I. CVD reactions for producing titanium nitride. \*\*\*=excellent, \*\*=good, \*=fair, uns=unsatisfactory, n/a=data not available.

Ti precursor N precursor	TiCl <sub>4</sub> NH <sub>3</sub>	TiCl <sub>4</sub> MeHNNH	TiBr <sub>4</sub> NH <sub>3</sub>	TiI <sub>4</sub> NH <sub>3</sub>	Ti(NMe <sub>2</sub> ) <sub>4</sub> none	Ti(NEt <sub>2</sub> ) <sub>4</sub> NH <sub>3</sub>
liquid precursor	***	***	***	*	***	***
inexpensive	***	*	**	**	*	*
stable in storage	***	**	***	***	***	***
non-flammable	**	*	**	**	*	*
non-toxic	*	uns	*	*	**	**
non-corrosive	*	*	*	*	**	**
volatile	***	***	***	*	**	*
fast vaporizing	***	***	***	*	**	*
stable vapor	***	***	***	**	**	**
low CVD temp.	*	**	**	**	***	***
deposition rate	***	***	***	***	***	***
film purity	*	**	**	**	*	***
conductivity	***	***	***	***	*	**
step coverage	***	***	n/a	***	***	**
byproducts	*	uns	*	*	**	**

Thus none of the previously-studied reactions fully meets all the criteria we have discussed as being desirable in a CVD reaction for producing titanium nitride. In the remainder of this paper we present new data on CVD of TiN by another reaction.

#### CHEMICAL VAPOR DEPOSITION EXPERIMENTS WITH TITANIUM TETRABROMIDE AND AMMONIA

A CVD process for titanium nitride using titanium tetrabromide has been patented, but process details have not been reported.<sup>10</sup> In this paper we report the successful use of CVD to form TiN from titanium tetrabromide and ammonia.

One difficulty in using TiBr<sub>4</sub> is that it is a very moisture-sensitive solid at room temperature. Because it is a solid, liquid injection systems cannot be used to vaporize the TiBr<sub>4</sub>. The entire reservoir and pump could be heated to temperatures above the melting point of TiBr<sub>4</sub>. However, refilling the reservoir would still be quite inconvenient, because it must be done in a dry atmosphere, such as a glove box. Also, transfer of solids is inconvenient to automate.

A more convenient liquid source for TiBr<sub>4</sub> can be formed by dissolving the material in liquid bromine, in which it is highly soluble. At 20 °C, a saturated solution contains about 88 weight per cent TiBr<sub>4</sub> and only 12 weight per cent bromine. At lower temperatures, the solubility decreases slightly, according to the data given in Table II.

Table II. Solubility of titanium tetrabromide in solution in liquid bromine, as a function of temperature.

Temperature °C	TiBr <sub>4</sub> content weight %	Br <sub>2</sub> content weight %
20	88	12
15	85	15
8	80	20

Increased pressure also lowers the solubility, because the density of the solid TiBr<sub>4</sub> is greater than that of the solution. A bromine solution of TiBr<sub>4</sub> also provides a convenient way to fill a bubbler with TiBr<sub>4</sub>. After filling, the very volatile solvent bromine may be removed easily by fractional distillation from the bubbler.

As a carrier gas, we used nitrogen gas boiled off liquid nitrogen, containing less than 0.5 ppm water or oxygen, which was then passed through a purifier that reduced the water and oxygen content below 0.1 ppm. Purified nitrogen flowed at a rate of 0.4 L/min through the titanium bromide bubbler, which was held at a temperature of 72 °C. The ammonia flow rate was 34 sccm, diluted by 10 L/min of purified nitrogen. These gas flows were controlled by mass flow controllers.

These two gas mixtures were separately preheated to a temperature of about 200 °C. This preheating is necessary to avoid adduct formation, which we found to occur if the gas mixtures are not preheated to a temperature of at least 150 °C. The two gas mixtures are then combined inside a 5 mm ID borosilicate glass tube just before it widened into a 22 mm ID glass tube. The temperature of the substrate was estimated by a thermocouple suspended next to the substrate inside the Pyrex tube. The actual substrate temperature is not very certain, because the high gas flow through the reactor caused significant cooling of the substrate. In future work, we plan to control and measure the substrate temperatures more carefully. The deposition time was five minutes. Then the glass or silicon substrate was cooled in a flow of pure nitrogen through the glass tube.

Shiny, golden films adhered strongly to the substrates. Analysis of the deposited films by Rutherford Backscattering Spectroscopy (RBS) showed that they consisted mainly of titanium nitride, along with small amounts of bromine, and sometimes iron. Samples prepared at temperatures near 500 °C had a bromine content of about one atomic per cent. Substrates placed close to the gas inlet were cooled to lower temperatures, and had a dark appearance and higher bromine contents.

The iron contamination of some of the samples probably arose from corrosion of stainless steel in the bubbler or delivery lines. The stainless steel should be replaced by nickel alloys such as Inconel™ or Hastelloy C™, or by fluorinated polymers, such as Teflon™, which resist corrosion by this solution.

The RBS data determines the mass deposited per unit area. We have not yet independently measured the thickness or density of the films. By assuming a typical film density of 4 g/cc, we can convert the RBS data to an average film growth rate of about 17 nm/min. Also using these thickness estimates, the resistivity was found to be about 200  $\mu\Omega$ -cm, which should be low enough to make satisfactory contact to silicon microelectronic devices.

## CONCLUSIONS

CVD reactions for TiN each have advantages and disadvantages. The CVD reaction of titanium tetrabromide with ammonia meets most of the requirements for microelectronic applications of titanium nitride, and merits further study to see if can meet all the requirements in a production reactor. A liquid solution of TiBr<sub>4</sub> in Br<sub>2</sub> is a convenient liquid source for vaporizing the TiBr<sub>4</sub>, although this solution needs corrosion-resistant materials to handle it. The deposited TiN has low electrical resistivity, but does retain a per cent or so of bromine impurity. This bromine content is well below the threshold level of chlorine contamination (3 atomic per cent) that caused corrosion in aluminum layers adjacent to the titanium nitride,<sup>4</sup> so the bromine in this TiN layer is not expected to cause corrosion.

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