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Plasma enhanced chemical vapor deposition of titanium diboride films

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the BF_2^+-implanted ones. In Fig. 4, the sheet resistances of Ti on unimplanted and 5×10^{14} and 6×10^{15} BF_2^+ cm^{-2} implanted silicon substrates are shown as a function of annealing temperature for time period of 30 min. After a 650 °C anneal, the sheet resistance dropped to 0.75–2.5 $\Omega/\square$, while, after annealing at 700 °C, resistance values of 0.7–0.8 $\Omega/\square$ resulted. Annealing at higher temperatures did not significantly change the sheet resistance. Apparently, the presence of a high concentration of boron and fluorine in the silicon did not affect the silicide formation and other characteristics. Such is not the case for titanium silicide formation on N^+-doped silicon.[9,10]

In summary, thin-film interaction between 1000-Å-thick titanium and BF_2^+-implanted, (100) silicon substrates was investigated. Annealing at 650 °C for 30 min resulted in an incomplete conversion to $TiSi_2$, leading to a titanium-rich (Si/Ti ~ 1.6) silicide layer on top while annealing at 700 °C or higher resulted in near-stoichiometric silicide (Si/Ti of 2.0–2.1). Boron was redistributed into the silicide layer and then was lost into the ambient during annealing while fluorine was segregated onto the silicide/silicon interface. Sheet resistance decreased to 0.7 $\Omega/\square$ after annealing at 700–900 °C.

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Plasma enhanced chemical vapor deposition of titanium diboride films

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Thin films of titanium borides were deposited at temperatures from 480 to 650 °C using a glow discharge and feed gases of $TiCl_4$, BCl_3, and H_2. High quality films have been obtained that are smooth, shiny, and crack-free; they have as-deposited resistivities as low as 200 $\mu\Omega$ cm. Films deposited with these moderate conditions have comparable properties to films deposited at high temperatures. These films have potential use as diffusion barriers or in other applications requiring a conducting refractory material.

Titanium diboride is a refractory material with high electrical conductivity and chemical stability. These properties make this material attractive for use as a diffusion barrier for integrated circuit metallization.[1,2] As far back as 1969,[2] TiB_2 has been suggested as a possible diffusion barrier, though since then little or no work has been reported on using it for this application. This may, in part, result from the lack of methods of producing high quality films of TiB_2 under conditions suitable for integrated circuit processing. Furthermore, the requirements for very large scale integrated circuit development impose even more stringent limitations on the commonly used deposition techniques: high-temperature processing must be minimized and step coverage quality must remain high. Plasma enhanced chemical vapor deposition is a potentially practical method for producing high quality TiB_2 films at moderate temperatures (< 650 °C) and with good step coverage.

Films of titanium diboride are usually deposited by chemical vapor deposition (CVD) at temperatures > 900 °C.[3] The overall reaction is

$$TiCl_4 + 2\,BCl_3 + 5H_2 \rightleftarrows TiB_2 + 10\,HCl$$

and the forward reaction becomes thermodynamically favored at temperatures above about 900 °C.[3] Studies have also been reported[3] wherein diborane is used in the reaction

$$TiCl_4 + B_2H_6 \rightleftarrows TiB_2 + 4\,HCl + H_2.$$

Although the thermodynamics for this reaction are favorable, the reaction kinetics prevent low-temperature depositions, and films deposited at temperatures less than about 700 °C are boron rich. Going to still lower temperatures (below 600 °C) yields soft noncohesive films.

Physical vapor deposition processes, such as evaporation[4] and sputtering,[5] have also been used for producing films of TiB_2. These processes can, of course, allow low deposition temperatures, but are of limited use since they require high-temperature anneals and have poor step coverage.

This letter shows that titanium boride films can be formed by plasma enhanced chemical vapor deposition (PECVD) at temperatures as low as 480 °C from mixtures of $TiCl_4$, BCl_3, and H_2; in addition, deposition rates for varying deposition parameters are reported along with resistivity and chemical properties of the films.

The films were deposited in a parallel-plate reactor contining stainless-steel electrodes. Substrates were placed on the lower electrode and heated with a resistance heater while temperature was monitored with a thermocouple placed inside the electrode. Feed gases were introduced to the reactor through a hole in the center of the top electrode; product gases exited the system via a port in the bottom of the reactor leading to a liquid nitrogen trap and mechanical vacuum pump.

Vapors of titanium tetrachloride, a liquid with a vapor pressure of 10 Torr at 20 °C, and boron trichloride entered the system at about 1 and 2 standard cubic centimeters per minute (sccm), respectively. The hydrogen flow was 10 or more sccm. The gases reacted in a 15-MHz glow discharge operating at 0.3 Torr and 20-W power applied to the top electrode using a Heathkit transmitter (Model DX-100B) and a matching network.

The films were deposited onto substrates of sapphire, pyrex, quartz, *p*-type silicon, and thermally oxidized silicon (0.3 μm of oxide). A four-point probe provided the film sheet resistance measurements, and film thickness was obtained with a stylus technique using a Sloan Dektak II. Film structure and composition were examined with x-ray diffraction and Auger electron spectroscopy (AES).

Attempts to deposit TiB_2 at room temperature (i.e., unheated electrodes) and at 60 °C were unsuccessful. At these temperatures, a violet colored film formed on the substrates, the electrodes, and the reactor walls. This material is believed to be primarily $TiCl_3$, based on reported[6] properties of the material. On exposure to air, the violet films turned white or transparent, depending on the thickness of the film.

At deposition temperatures of 480 °C and higher, a reflective metallic film formed on the substrates and bottom electrode, though, as before, the violet film deposited onto the cooler surfaces, including the top electrode. Figure 1 shows deposition rates for the metallic film at temperatures ranging from 480 to 650 °C. Deposition rates ranging from 40 to 70 Å per minute occurred for the conditions of 20-W rf power (0.25 W per square centimeter), 0.3 Torr, and $TiCl_4$, BCl_3, and H_2 flows of 1, 2, 10 sccm, respectively. Further studies of the influence of hydrogen flow rate on the deposition rate showed a gradual increase in deposition rate with increase in hydrogen flow rate. These results are summarized in Fig. 2: at 600 °C, the deposition rate increased by about 50% when the hydrogen flow rate was increased from 10 to 30 sccm. Further increases in the deposition rate can be achieved by increasing the rf power input and by increasing the flow rates of BCl_3 and $TiCl_4$.

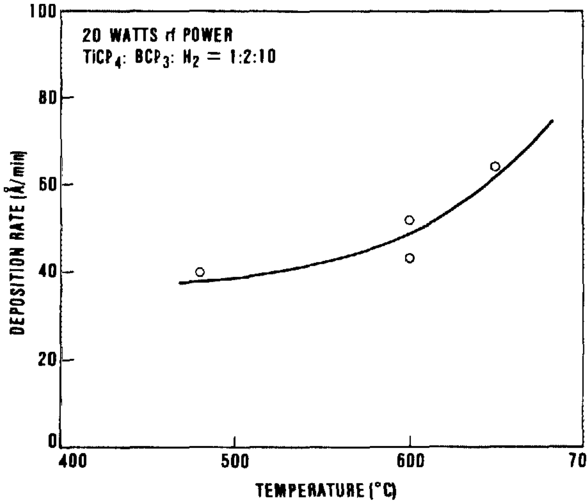

FIG. 1. PECVD TiB_2 deposition rate dependence on substrate temperature.

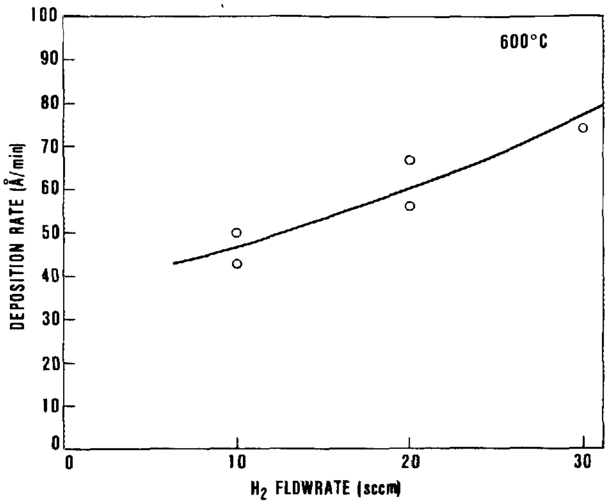

FIG. 2. PECVD TiB_2 deposition rate dependence on hydrogen flow rate.

Figure 3 shows an Auger electron spectrum of the bulk titanium diboride film deposited onto silicon at 600 °C from a feed gas composition of about 1:2:20 sccm of $TiCl_4$, BCl_3, and H_2, respectively. Boron and titanium appear as the primary components; there are also trace amounts of oxygen and carbon (presumably due to poor vacuum conditions or contaminants in the feed gases); the neon peak results from using neon to sputter clean the boride surface. Figure 4

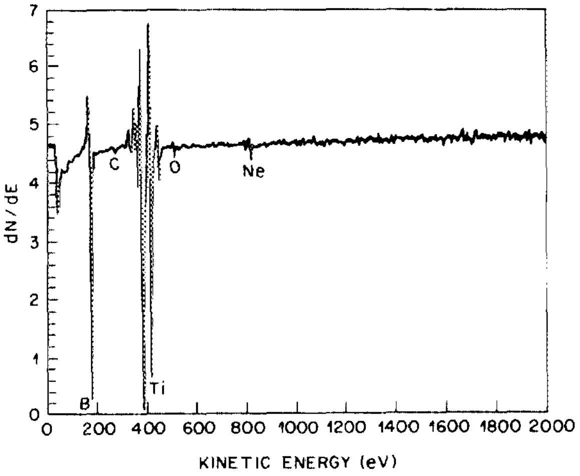

FIG. 3. Auger electron spectrum of a titanium boride film deposited onto silicon at 600 °C using $TiCl_4$, BCl_3, and H_2 flowing at 1, 2, and 20 sccm, respectively.

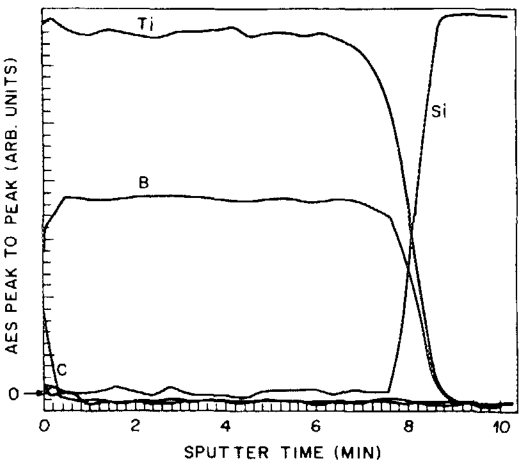

FIG. 4. Composition profile from Auger electron spectroscopy for the titanium boride film described in Fig. 3.

shows that the composition profile through the film is uniform except at the surface and near the silicon interface.

Near the surface, the amounts of carbon and oxygen drop sharply, whereas the boron shows a large increase, and the titanium shows little change. The transition from the boride to the silicon substrates appears to be sharp, suggesting there is little interaction between the boride and the substrate during deposition.

For films deposited at 600 °C and above, the Auger spectra do not show any identifiable amounts of chlorine. However, low concentrations of chlorine may be masked by the overlap that occurs for the chlorine and the boron Auger peaks. X-ray fluorescence measurements on films deposited at 600 °C indicate that chlorine is present but only at trace levels. Presumably, the chlorine content of the films increases with decreases in the deposition temperature, as is evident by the appearance of $TiCl_3$ at deposition temperatures below 480 °C. Hydrogen incorporation into the films probably follows a pattern similar to that as for chlorine: preliminary studies show no significant amounts of hydrogen in films deposited at 600 °C. Further work on film composition is in progress.

Composition and structural properties of two of the films (about 1500 Å thick) were also examined using x-ray diffraction. Both films were deposited at 600 °C; one onto fused quartz, the other onto silicon. For 2θ angles ranging from 10° to 60° (Cu K_α radiation), the film on the quartz substrate showed no diffraction peaks attributable to a crystalline phase. The film deposited onto the silicon substrate showed one diffraction peak indicating it was at least partially crystalline. This peak, centered at 45°, has an equivalent d spacing of 2.01 Å and thus corresponds to the d spacing, 2.03 Å, for the most intense peak for crystalline titanium diboride.[7]

Resistivities for the PECVD titanium borides depend on the deposition conditions, and generally, the lowest resistivities occur for the highest deposition temperatures and H_2 flow rates. Under the conditions examined in this study, the resistivities ranged from about 200 to 450 $\mu\Omega$ cm. For comparison, reported resistivity data for TiB_2 films are summarized in Table I. TiB_2 films deposited by evaporation and sputtering had resistivities[4,5] lower than that for the as-deposited PECVD films, but the evaporated and the sputtered films had received high temperature (> 950 °C) anneals; the sputtered films had an as-deposited resistivity that was greater than that for the PECVD films. Conceivably, the resistivities of the PECVD films could be reduced further by high-temperature anneals and by further optimization of the deposition conditions. However, for application as a diffusion barrier, the as-deposited resistivities of about 200 $\mu\Omega$ cm are reasonable: other transition metal compounds with similar resistivities, such as nitrides and carbides, have been[8,9] studied as possible diffusion barriers.

TABLE I. Resistivity data for TiB_2.

Preparation	Resistivity ($\mu\Omega$ cm)
Single crystal[a]	7
Evaporated[b]	
annealed (950 °C)	30
Sputtered[c]	
as deposited	500
annealed (1050 °C)	150
PECVD[d]	
as deposited	200

[a] V. N. Gurin and V. S. Sinelnikova, in *Boron and Refractory Borides*, edited by V. I. Matkovich (Springer, NY, 1977), pp. 377–389.
[b] Reference 4.
[c] Reference 5.
[d] This study.

High quality films of titanium borides can be deposited by PECVD at moderate temperatures (< 650 °C). The films are smooth, shiny, crack-free, and highly conductive, and as such may be suitable for use as diffusion barriers for integrated circuit metallization. However, much work needs to be done to determine the high-temperature interactions between the titanium borides and silicon, silicides, and aluminum. Also, the patternability of the boride films must be investigated.

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