

Chemistry of titanium dry etching in fluorinated and chlorinated gases

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Abstract - The chemistry of the dry etching of titanium thin films has been investigated in fluorinated and chlorinated environments. In CF_4/O_2 plasma the hard native stoichiometric oxide, TiO_2 , always present on the titanium surface, results in a non-reproducible induction time. During etching the surface of titanium is covered by a highly fluorinated layer which protects the metal by the reaction with oxygen. Chlorine is not able to remove the native oxide unless drastic conditions are realized. Once this layer is removed with fluorine, the reaction with molecular chlorine proceeds also without plasma. Fluorine atoms act by making the titanium surface more reactive towards chlorine.

INTRODUCTION

Titanium and its compounds are increasingly being utilized in many new applications which require dry etching processes, such as microelectronics and optoelectronics manufacturing. While a deep knowledge on titanium mechanical and chemical properties has been gained since the beginning of this century, for its utilization in metallurgy and as catalyst in organic chemistry, the dry etching behavior of titanium has not been carefully investigated. In this paper we will report on the reactivity of titanium in fluorine and chlorine containing environments, in those conditions where the chemical aspects are emphasized for the low energy and dose of charged particle bombardment.

Mostly the study has been performed by comparing the results of gas phase diagnostics and etch rate measurements with XPS-surface analyses after the treatment, without exposing the substrate to air. This has been accomplished by connecting under vacuum a plasma chamber to an XPS spectrometer (ref. 1). On our opinion, this experimental approach is very convenient in order to obtain information on the surface conditions when etching is performed in "real" systems, *i.e.* contaminated by chemicals and atmosphere, at the pressure currently utilized during the processes. Of course, the assumption that the surface is stable and does not change during the time needed for transferring the samples into the spectrometer must be done. Other experimental approaches, such as the simulation of plasma with ion, radical and molecular beams, even though are characterized by some advantages, such as the capability of performing surface analysis during the treatment and to carefully control the extent of each variable, suffer the disadvantage that the operating conditions are very different from the real ones. This is a key point when one deals with very reactive substrates such as titanium. Titanium, in fact, acts as a sponge with several gases and forms stoichiometric and nonstoichiometric compounds, solid solutions, and adsorbed layers as a function of the temperature, pressure, exposure time, and surface contamination (ref. 2). In particular its interaction with oxygen (often present in real systems for leaks or wall desorption) results in a wide variety of compounds and in solid solutions (up to the 30 atomic % of oxygen can be dissolved in Ti-crystal). For long exposures to air the surface becomes deeply modified, and layers of "hard" quasi-stoichiometric TiO_2 , on a "soft" TiO_x layer (x decreases with the depth) grow on the sample surface (the adjectives hard and soft are used to qualify the extent of reactivity with the etchant species). The thickness of these modified layers depends on several factors. In general titanium can also incorporate non-

metal atoms in the octahedral sites of the metal lattice where they assume a slightly negative charge becoming strongly bonded but mobile, and expanding the lattice structure. The etching characteristic of titanium is further complicated by the high reactivity of H₂O with the etch products which leads to the formation of passivating oxide and/or oxo- or hydroxo-halides layers.

ETCHING IN FLUORINE CONTAINING GASES

It has been reported that molecular fluorine can spontaneously react with clean titanium and TiO₂ at temperatures higher than 200 and 350°C, respectively, resulting in TiF₄ production. In glow discharges containing fluorine atoms, more reactive than molecules, the reaction occurs also at room temperature. The process of titanium etching in fluorinated plasma (e.g. CF₄/O₂ glow discharges) consists in three successive steps: 1) the ablation of the "hard" stoichiometric TiO₂ oxide; 2) the etching of the "soft" non-stoichiometric TiO_x, 3) the etching of metallic titanium. The etching rate during the first step is negligible, then it increases in the second step.

This is because, in close analogy with aluminum in chlorine containing plasmas, the native stoichiometric oxide does not easily react with etchants. Induction time turns out to depend on the thickness of TiO₂ layer. This can be better appreciated by considering the composition of the etched surface, as detected by XPS analyses, reported in Fig. 1 after different plasma exposure periods. Until the TiO₂ feature (Ti_{2p} doublet at 459 and 465 eV) is present, the etch rate is negligible. When the stoichiometric oxide is removed the surface is covered by a highly fluorinated layer composed by TiF₃ and TiF₄, in which some fluorine is trapped as it can be deduced both by the high fluorine - to - titanium atomic ratio (F/Ti > 4) and by the shape of the F_{1s} XPS peak. The thickness of the modified layer is not very reproducible, values in the range 30-50 Å have been detected. If the process is performed in reactive ion etching conditions, the surface is composed only by TiF₃, no evidence of trapped fluorine have been detected and the thickness of the modified layer is lower (15-20 Å) (ref. 3). The surface fluorinated layer is enough stable, however it slowly reacts with moist to form oxohalides and/or TiO₂, and it is inert towards molecular or atomic oxygen even when a light positive ion bombardment is present. The overall process is controlled only by the fluorine atom concentration, and it is not appreciably influenced by contaminants even when their concentration is high. By increasing the oxygen percent in CF₄ plasma, while the oxygen atom concentration continuously increases, that of fluorine goes through a maximum for the dilution effect and for the homogeneous reaction:



Changing the feed composition, therefore, is a convenient way to vary the relative concentration of fluorine and oxygen atoms in a wide range for studying the competition between oxidation and fluorination. It is interesting and rather surprising, at least for the authors, that in the case of titanium it has been found that oxygen does not compete at all with fluorine in the reaction with the surface, unlike Si and W. In fact, the trend of titanium etch rate and that of fluorine atom concentration, obtained by Actinometric Optical Emission Spectroscopy, fairly well coincide

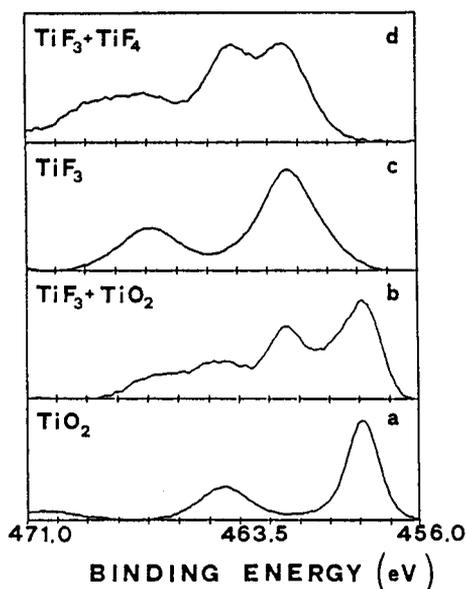


Fig. 1. XPS-Ti_{2p} doublet feature after different treatment time in CF₄ 100 % plasma (very soft conditions): a) untreated Ti surface (TiO₂); b) 1 minute of treatment; c) 15 minutes; d) 60 minutes. The F-to-Ti ratio detected for sample d with a take off angle of 45° is 4.3.

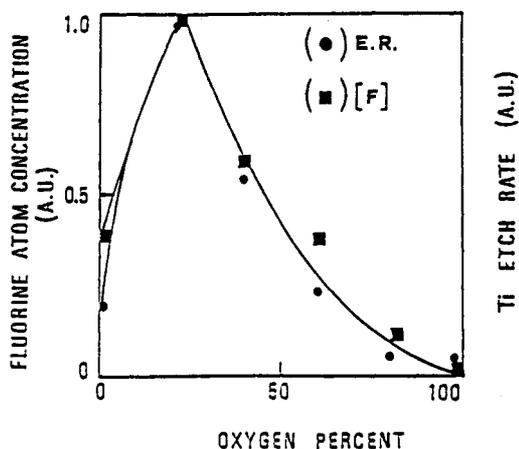


Fig. 2. Actinometric fluorine atom concentration and titanium etch rate trends as a function of oxygen percent in CF_4 plasma.

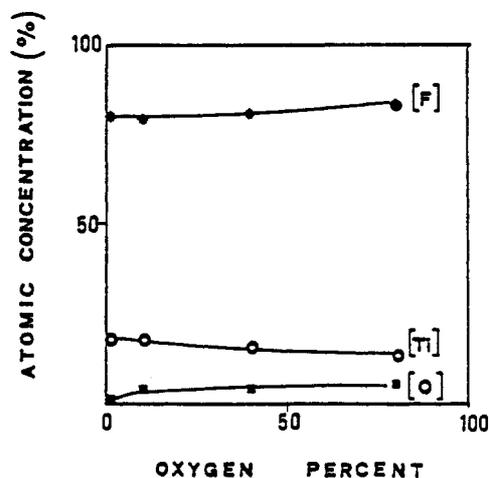


Fig. 3. Surface composition obtained by means of XPS quantitative analysis for samples treated in $\text{CF}_4\text{-O}_2$ plasmas by varying the feed composition.

(Fig. 2); the two maxima are not shifted as found in the same gas mixture for silicon (ref. 4) and tungsten (ref. 5). The composition of the etched surface, on the other hand, is not appreciably affected by the plasma composition, even when the fluorine - to - oxygen ratio is varied in a wide range (Fig. 3). When fluorine atoms stick on titanium surface they are very hardly removed (see next section for the case of chlorine) unless they leave the sample as part of etch products. The thick "protective" fluorinated layer also acts by reducing the effect of low energy positive charged particle bombardment. The etch rate of titanium, in fact, shows a moderate increase when the substrate bias voltage is varied from floating potential to -120 V, the variation is lower than that detected for silicon and tungsten under similar conditions. To obtain vertical etching, drastic conditions, as those realized in reactive ion etching operation, or appropriate gas mixtures able to supply the surface with sidewall inhibitors, must be utilized.

The etching rate increases with temperature and shows an apparent activation energy, EA, of 9 Kcal/mol in the range $20\text{-}200$ °C. By the comparison of EA with the heat of sublimation of TiF_4 , 22.4 Kcal/mol, it can be stressed that TiF_4 sublimation is not the rate limiting step of the process neither could be the volatilization of other titanium fluoride, characterized by too low volatility to support the detected etch rates. The bottleneck of the process, therefore, in analogy with what reported for RIE condition, is most reasonably, the last step of fluorination, in which the volatile TiF_4 molecule is produced from TiF_3 . The fact that some TiF_4 is left on the surface after the process is not in disagreement with this conclusion. In fact, once some molecules of TiF_4 are formed, they can remain in part adsorbed on the surface by utilizing some of the empty d orbitals of titanium. If the process is conducted at higher temperature, or strong ion bombardment is present (as in the case of RIE operation), the probability of finding TiF_4 adsorbed on the etched surface is dramatically reduced.

ETCHING IN CHLORINE CONTAINING GASES

Even though the volatility of TiCl_4 is much higher than that of TiF_4 (the vapor pressure of TiCl_4 is about 100 torr at room temperature) the reaction of chlorine with titanium presents several problems. It is difficult to initiate, since titanium oxides (also the non stoichiometric TiO_x) are not chemically removed by chlorine atoms and/or molecules, and the etch products are very reactive with the residual gas of the vacuum system or with the atomic oxygen, forming passivating oxidized layers which tend to stop the reaction. The inertness of the the oxide towards chlorine atoms and molecules is more reasonably due to the fact that chlorine does not chemisorb appreciably on it even when a soft ion bombardment is present. Also the addition of BCl_3 or CCl_4 to the gas mixture has not been successful for oxide remotion, unlike aluminum. The different reactivity of chlorine with respect to fluorine is not surprising, it has been reported, in fact, that the pure chemical reaction between TiO_2 and Cl_2 needs high temperature (350 °C) and the

presence of a reducing agent, such as carbon (grafite), to occur (ref. 2) while that of fluorine requires only high temperature. Once the oxidized layer has been removed (for instance with the aid of strong ion bombardment), the plasma etching of titanium can proceed, provide the level of residual gas in the reaction chamber is kept low.

The spontaneous reaction between chlorine and clean titanium surface (without plasma) has been studied by several authors, however the results are not always in agreement, indicating that the reaction is strongly influenced by several parameters and by the surface conditions and cleaning procedures. Chlorine dissociatively adsorbs on the Ti surface with a non activated process (ref. 6) and forms several monolayers of adsorbed chlorine on smooth, defect free single crystal surfaces and halides species on foils or damaged surfaces (ref. 7-9). It seems established that to form the halide layer the titanium surface must be subjected to ion bombardment during or before the exposure. Most reasonably, ions provided the surface with the energy needed in the first step of chlorination: $\text{Ti} + \text{Cl} = \text{TiCl}$, which is endothermic and/or make the surface more reactive by creating defects in its structure (ref. 9).

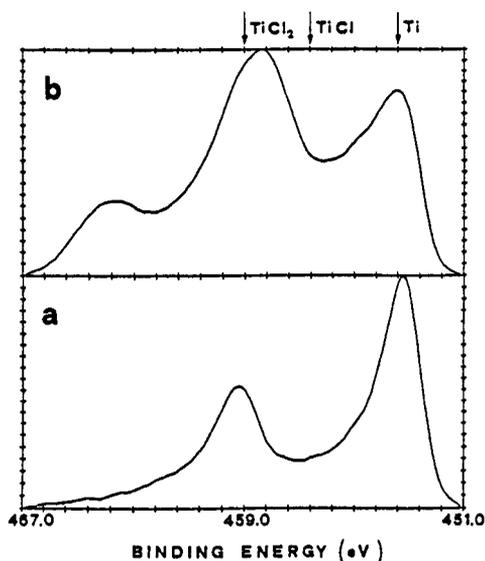


Fig. 4. XPS- Ti_{2p} doublet feature: a) after cleaning by means of ion beam sputtering, and b) after 20 minutes of exposition to Cl_2 (100 mtorr).

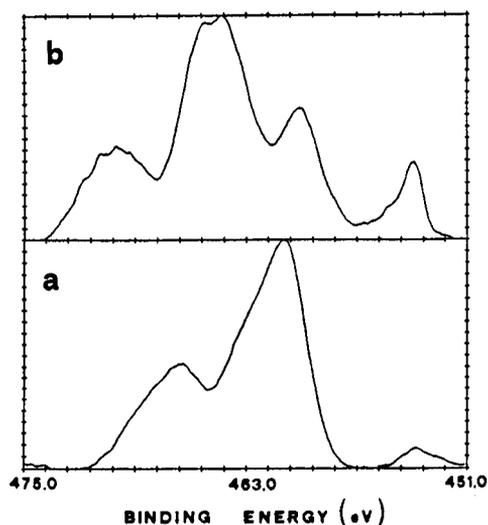


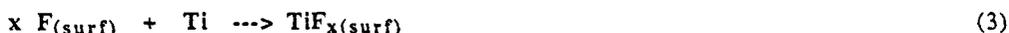
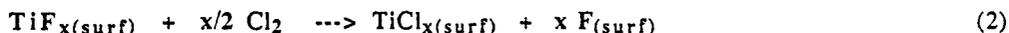
Fig. 5. XPS- Ti_{2p} doublet feature: a) after treatment in CF_4 plasma to remove the surface oxide, and b) successive etching in Cl_2 at 100 mtorr without plasma.

Of course the effect is better detected when ion bombardment and chlorine exposure occur contemporaneously. So far, even if on the basis of thermodynamic considerations the reaction between chlorine molecule and nonoxidized titanium should occur spontaneously, no appreciable etching has never been revealed without plasma or in the absence of ion bombardment.

The surface of a Ti sample, cleaned by means of ion beam sputtering, when exposed to a chlorine environment is modified as evident in Fig. 4. The XPS doublet of metallic titanium (a 10 % of oxygen is still present on the surface) shows the appearance of TiCl and TiCl_2 features. These features are also evidenced (the second one in particular) when before the chlorine exposure (20 minutes at 100 mtorr), the surface oxide is removed by means of a CF_4 plasma treatment (Fig. 5); in any case the main peaks are those of TiF_4 and TiF_3 . The approximate quantitative analysis (performed without correction for the sampling depth of each signal) has shown that the composition of the surface whose Ti_{2p} spectrum is reported in Fig. 5 is: F, 64 atomic %; Cl 20 atomic %; Ti 15 atomic %; carbon and oxygen content is complexively lower than 1 atomic %. Preliminary depth profiling investigations, on the other hand, have clearly shown that the chlorine concentration drastically decreases after the remotion of the topmost layers, while the penetration of fluorine is much deeper. The fact that surprisingly fluorine is left on the surface even after long treatment time with chlorine, is an additional evidence of the high stability of the fluorinated surface.

When titanium surface is fluorinated and no oxide is present, chlorine quickly etches titanium, even in the absence of plasma, with an etching rate as high as 1000 Å/min (compared to 200 Å/min in CF₄ plasma).

It can be concluded that fluorine atoms must play a very important role in the overall process since they remain on the surface until the end of chlorine treatment (Fig. 5) and allow the reaction of titanium with chlorine to occur even without ion bombardment superimposition. Two explanations are in agreement with the experimental results: 1) fluorine catalyzes the reaction with chlorine creating very reactive sites and defects on the surface structure which lower the energy required for the first endothermic step of chlorination of titanium, or 2) it completely changes the way the first chlorination occurs. The second hypothesis means that chlorine could react with fluorinated titanium taking the place of fluorine, which remains on the surface and reacts with other titanium atoms as reported in Eq. 2 and 3.



The first step of the reaction of chlorine with titanium could, therefore, occur through some of the same steps of the reaction of fluorination, of course the reactions must follow different paths before the rate limiting step of the fluorination is attained, otherwise it could not be possible to explain the higher etching rate obtained in chlorine without plasma.

Also in the Reactive Ion Etching of titanium in chlorine containing plasma, the beneficial effect of fluorine addition on the etching rate has been reported (ref. 10). In this case the strong ion bombardment supplies enough energy and/or surface damage to remove the surface oxide and to allow the reaction to proceed. The etching rate increases two or three times when 10 % of a fluorinated gas is added to the feed and an amount of fluorine comparable to chlorine is left on the surface after the treatment. This is a further evidence of the catalytic effect of fluorine.

Metallic titanium is protected by the fluorinated layer from the oxidation by reaction with oxygen (principally) and water (if its content in the residual gas is low) since fluorinated titanium is less reactive respect to pure metal and, particularly, respect to titanium chlorides. In any case, while the oxygen content of the vacuum chamber is not one of the main concern (oxygen can also be contained in the feed) the water contamination must be very low. The etch product, TiCl₄, in fact, does not react at all with molecular oxygen at low temperature, but is highly hygroscopic and reacts with water forming oxochlorides and hydrated oxides which can cover the surface and stop the etching. If the experimental system is not particularly protected from leaks or atmosphere exposure this problem can be serious and in few minutes the etching rate can approach zero. As for the case of aluminum an appropriate water scavengers, such as BCl₃, can be added to the feed. Mass spectrometric investigations, in fact, have clearly shown that the water content of a system systematically exposed to air for loading the samples, is drastically reduced when the feed contains 10 % of BCl₃ (the oxygen content is unaffected).

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REFERENCES

1. R. d'Agostino, F. Fracassi, C. Pacifico, submitted for publication.
2. D.L. Kepert, The Early Transition Metals, p. 61, Academic Press, New York (1972).
3. S.W. Robey, M.A. Jaso, and G.S. Oehrlein, J. Appl. Phys., **65**, 2951 (1989).
4. C.J. Mogab, A.C. Adams, and D.L. Flamm, J. Appl. Phys., **49**, 3896 (1978).
5. F. Fracassi, and J.W. Coburn, J. Appl. Phys., **63**, 1758 (1988).
6. T. Smith, J. Electrochem. Soc., **119**, 1388 (1972).
7. P.R. Watson, S.M. Molker, and J. Mischenko, III, J. Vac. Sci Technol. A, **6**, 671 (1988).
8. W.L. O'Brien, T.N. Rhodin, J. Vac. Sci. technol. B, **7**, 1244 (1989).
9. W.L. O'Brien, T.N. Rhodin, and R.C. Rathbun, J. Chem. Phys., **89**, 5264 (1989).
10. K. Blumenstock, and D. Stephani, J. Vac. Sci. technol. B, **7**, 627 (1989).