

NOTE ON THE FORMATION OF SURFACE CARBIDES

P.SELVAM

Laboratory of Interdisciplinary X-ray Crystallography, University of Geneva, 24, Quai E. Ansermet, CH-1211 Geneva 4 (Switzerland) and Department of Chemistry, Indian Institute of Technology, Madras 600 036, Tamil Nadu (India)

B. VISWANATHAN and V. SRINIVASAN

Department of Chemistry, Indian Institute of Technology, Madras 600 036, Tamil Nadu (India)

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ABSTRACT

Features of the effect of ion bombardment and its influence on the composition of solid surfaces are considered. During ion bombardment, not only does cleaning (sputtering) of the surface take place, but the formation of carbides through the implantation of carbon from contamination also occurs. Such species were recognized clearly from their chemical shifts of XPS on intermetallic compounds, namely LaNi_5 , CaNi_5 , TiFe , Mg_2Ni and Mg_2Cu and on the hydride Mg_2NiH_4 . These surface carbides, for example, can seriously restrict data analysis owing to their contribution to the core level alterations, and the rate of sputtering owing to their extreme hardness. However, ion bombardment would serve as an unusual method of preparation of some compounds which cannot be obtained by conventional means. Types of problems, methods and results of their investigation are described.

INTRODUCTION

The technique of XPS is widely employed with increasing regularity for characterizing the electronic structure of many solid-state systems of both outer-shell (valence level) and inner-shell (core level) photoelectrons. The surface sensitivity and the chemical specificity of the ejected electrons are well suited to elucidating the structure of complex species, making it an excellent approach in connection with ion bombardment methods. In particular, the presence of chemisorbed gases such as O_2 , H_2O (moisture), CO , CO_2 , etc. as well as unusual surface oxides exhibiting gross defect structures can yield a detailed understanding of the surface chemistry. Although ion bombardment is used universally for surface cleaning, either by itself or in combination with heating, the potential user should be aware of the artefacts that can be introduced by it [1-8]. These take the form of chemical and/or topographical changes induced at the surface or formation of new compounds by the recombination of the sputtered particles.

The technique of cleaning the surface by ion bombardment is, in principle, simple and straightforward. However, as remarked above, the chemical changes induced by the bombardment itself can be equally serious. They include reduction of compounds and persistence of elements in the material. In the former, more volatile elements such as oxygen in oxides, sulphur in sulphides etc. are lost (knock-off) preferentially during sputtering. Such loss is inevitably accompanied by a reduction in the oxidation state [1-5,7]. In the latter, light elements, particularly carbon, can be driven (knock-on) further into the material by direct impact from a primary ion and/or by indirect impact via an energy cascade [3-5,8]. Often the importance of such effects has not been noted in the literature, in particular for the latter effect. Ion bombardment, then, although certainly effective in removing the dirt from the surface, brings in its train some highly undesirable side-effects, of which some are accountable but others as yet are not. Nevertheless, the technique is so widely used that it is necessary to watch continually for the intrusion of artefacts during the sputtering of the samples.

Recently, we reported [9,10] on the surface properties of various hydrogen storage alloys and hydrides. Despite some promising and impressive observations, the formation of higher valent terminal oxides [9,10], lower valent sub-oxides [9,10], carbonates [11] and ion-induced carbides [8] at the surface created significant interest. In this report, we extend our previous work (XPS and AES) on the TiFe alloy [8] to other systems, and attention is paid especially to surface changes following bombardment with argon ions. The influence of such a process on the diffusion of impurities and on the chemical activity of the materials is also considered. The results show that upon sputtering, carbide species always exist on all the studied compounds. Incidentally, the formation of surface carbides has a relevance with respect to mechanisms involved in the methanation reactions [12-14] as well as their role in the hydriding reactions of hydrogen storage materials [15]. However, a basic understanding of sputtered carbon is crucially important as a result of the use of hard carbon films as abrasion-resistant coatings in magnetic recording applications [16].

EXPERIMENTAL

The intermetallic compounds LaNi_5 , CaNi_5 , TiFe, Mg_2Ni and Mg_2Cu and the hydride Mg_2NiH_4 were the same samples used in our earlier investigations [9,10]. The experimental conditions, techniques, procedures and the analysis have been discussed elsewhere in detail [7-10,17]. Here we report on the XPS results of the C1s region. The X-ray source used was an Mg anode and the ejected photoelectrons were measured with a pass energy of 50 eV in the case of TiFe, and a pass energy of 25 eV for the other compounds. All the measurements were carried out at room temperature in the as-received air-exposed

conditions as well as after different sputtering periods. The samples were subjected to argon ion bombardment with a beam voltage of 8 kV and a target current of $60 \mu\text{A cm}^{-2}$ for TiFe and $100 \mu\text{A cm}^{-2}$ for the other compounds.

RESULTS AND DISCUSSION

Figures 1–3 indicate the C1s spectra of various samples in the as-inserted state and with various sputtering times. The spectra of the as-received samples show signals due only to adventitious carbon at 284.5 eV (see the top lines in the figures), which is also used for calibration purposes. However, the spectra of unsputtered CaNi_5 (Fig. 1; right hand side, top spectrum) consist of more than one line, the hydrocarbon line at the left and the other lines originate

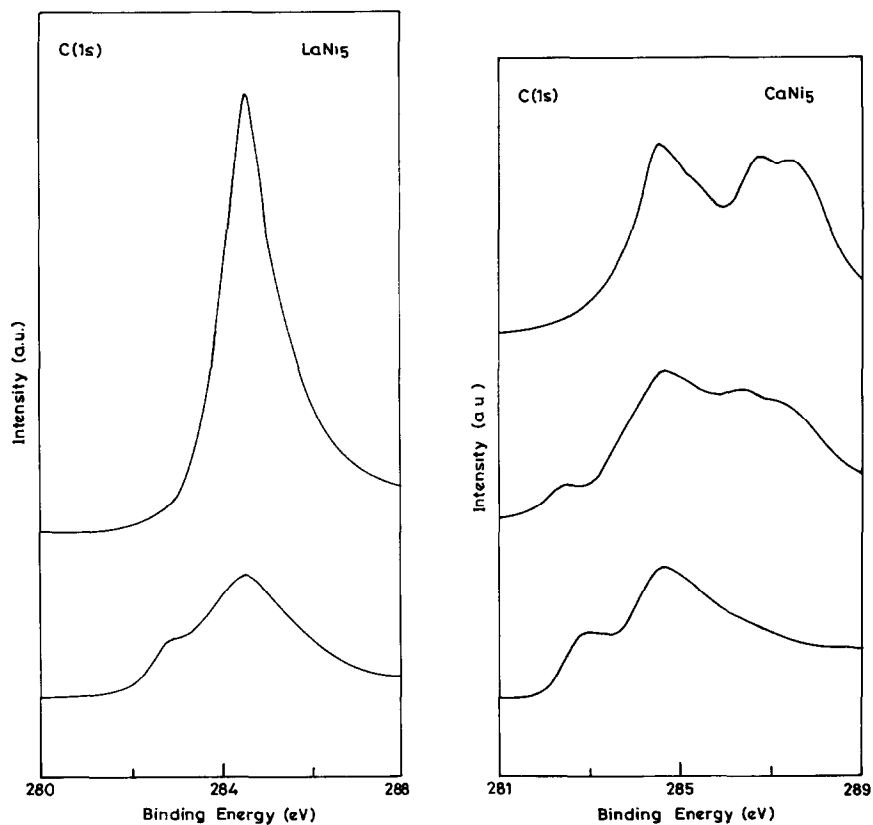


Fig. 1. Influence of argon ion bombardment on the formation of surface carbides. The first (top) lines represent initial contaminated surface. The subsequent lines are obtained after sputtering for different times. In the case of CaNi_5 (right), the peaks at higher binding energy side (next to reference carbon) are due to surface carbonates (see text). Sputtering periods (top to bottom): LaNi_5 (0 s; 300 s); CaNi_5 (0 s; 180 s; 900 s).

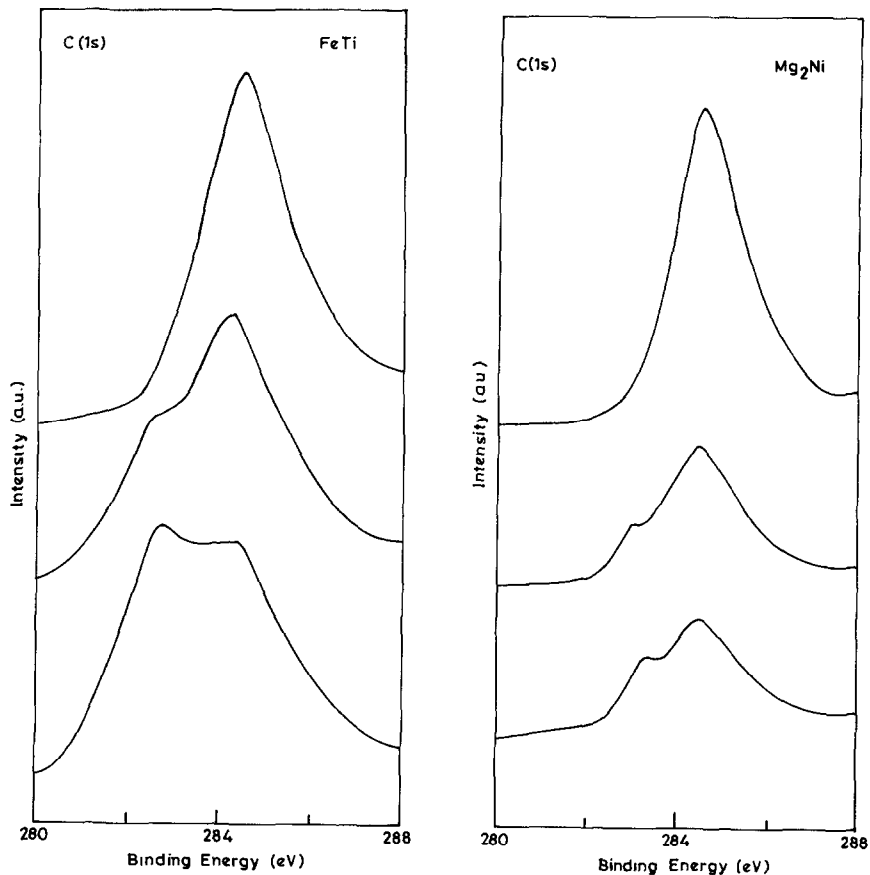


Fig. 2. Influence of argon ion bombardment on the formation of surface carbides. For description see Fig. 1. Sputtering periods (top to bottom): TiFe (0 s; 210 s; 510 s); Mg₂Ni (0 s; 300 s; 600 s).

from carbon in the carbonates [11]. These lines were normally found next to the reference carbon owing to the increasingly positive charge on the carbon atoms. In the case of the other systems, carbonate species also appeared but at slightly higher binding energy [11]. For the sake of convenience they are not included in the figures. Such contamination layers (and others) are removed periodically by argon ion bombardment. This, however, results (as in the present study) in the formation of additional features corresponding to a carbide-type species. They seem to be predominant (for thermodynamic reasons) in the case of the TiFe system (see Fig. 2). These signals can be assigned to either pure carbide- and/or oxycarbide-like species. The latter may be facilitated by the surface oxides initially present [8]. It should be noted that the component elements of the alloy TiFe are known to form a bulk carbide [18–20] and Ti,

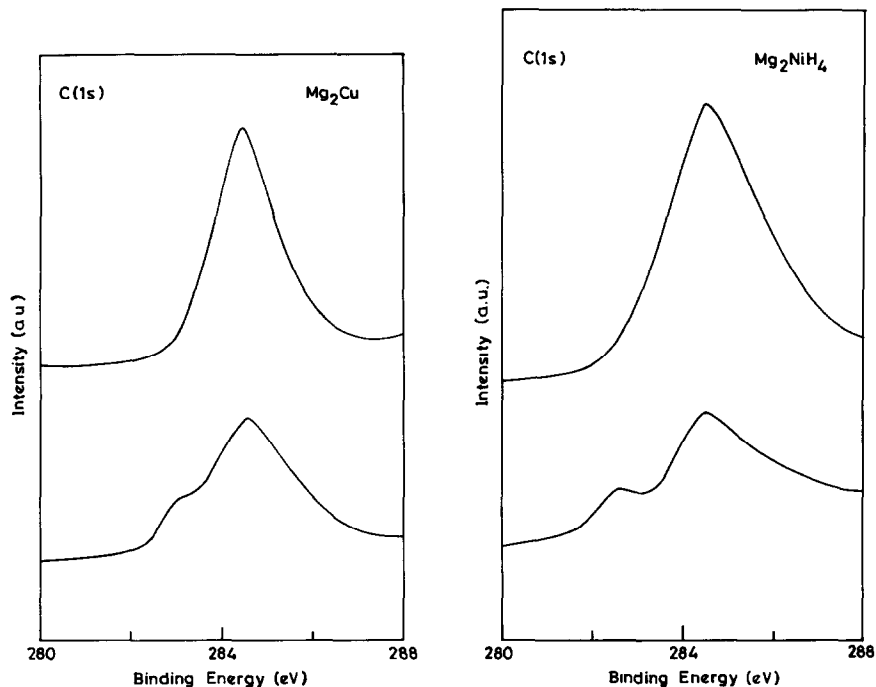


Fig. 3. Influence of argon ion bombardment on the formation of surface carbides. For further details see Fig. 1. Sputtering periods (top to bottom): Mg_2Cu (0 s; 480 s); Mg_2NiH_4 (0 s; 750 s).

in particular, is found to produce an oxycarbide in the presence of an oxidized surface [15].

The influence of ion beam irradiation on the surface of different samples is illustrated in Figs. 1–3. As can be seen from the figures by the appearance of a new signal to the left of the reference carbon signal, carbide layers build up slowly on increasing the time of sputtering. That is, the peaks have lower binding energy (shifted to $\sim 1\text{--}2$ eV) with reference to the hydrocarbon line. This behaviour shows clearly that on a sputtered surface, the ion beam stimulates the formation and build-up of carbidic-type species. The mechanisms involved are probably complex, involving interactions between adsorbed carbon species with an activated surface by the action of the ion beam. It is noteworthy that similar ion-induced effects, such as the formation of fluorides of Ti [3–5] and higher valent oxides of Ni [1,2] have already been proved. The appearance of new peaks (~ 282.5 eV), negative with reference to carbon (284.5 eV), of the sputtered samples indicate that carbon in carbides has a lower binding energy than that in hydrocarbons, as for oxides in the O1s region. This provides evidence that charge is transferred from the metal atom to the carbon atom in a similar way to charge transfer from the metal to the non-metal constituent in

related compounds such as borides, nitrides, oxides and fluorides [3–5,18–20]. The energy separation between the two lines ($\sim 1\text{--}2\text{ eV}$) is in good agreement with $C1s$ shifts reported for ion-induced metal carbides [3–5] and with carbides formed by the carburization of Ni and TiFe in a CO atmosphere [21,22]. However, as expected, the energy shifts are slightly more for the bulk carbides [18–20]. The results presented here are supported in a parallel investigation on the AES studies of the C *KLL* region of TiFe [8].

The XPS signals of the ion bombarded samples are complex in nature, mainly because of the binary composition of the systems and hence it is difficult to identify the actual species. Therefore, they are assumed to be carbides of the constituent elements of the alloys or a ternary carbide of the alloys themselves; even oxycarbide-type moieties could be responsible for such an observation as ternary carbides with oxygen are known [23,24]. The formation of the latter species may be facilitated by the surface oxides initially present [9,10]. However, the overall formation of carbides can be rationalized in terms of the reactivity and the influence of the radiation effect. The stability of the reaction product is one of the essential factors in discussing the different reactions. This is inferred from the Gibbs energy of formation (ΔG_f°) of the compounds. Hence, based on the thermodynamic considerations, one would expect the formation of TiC, CaC_2 and LaC_2 on TiFe, $CaNi_5$ and $LaNi_5$ surfaces, respectively. However, standard free energy considerations do not favour the formation of MgC_2 or Mg_2C_3 and the carbides of Fe, Ni and Cu, namely Fe_3C , Ni_3C and Cu_2C_2 (see Table 1). On the other hand, the existence of the latter compounds has been reported in the literature [12–14,23,24,26]. In particular Mg, and to the right of the transition series, carbides, have been synthesized or observed on the surface, although they cannot be made by the normal method of heating the metal and carbon together.

To illustrate, the carbides of Fe and Ni belong to the unstable interstitial alloys and are prepared by the carburization of the respective metals in a hydrocarbon atmosphere [12–14,23,24]. The carbides of Cu, commonly called

TABLE 1

Standard free energy of formation of certain carbides [25,26]

Compound	ΔG_f° (kJ mol ⁻¹)
MgC_2	+71.2
Mg_2C_3	+83.7
CaC_2	-64.5
TiC	-180.0
LaC_2	-72.4
Fe_3C	+79.5
Ni_3C	+133.1
Cu_2C_2	-

acetylides, are prepared by passing acetylene into ammoniacal solutions of the metal salts [27]. As many of these compounds are metastable they are usually produced by such indirect methods. The general methods of preparation of various carbides include the following [23, 24, 26].

The direct reaction of carbon either by melting or sintering with metals or metal hydrides in a protected atmosphere or in vacuo, e.g., carbides of groups II-A, IV-B, V-B and VI-B.

The direct reaction of the metal oxide and excess carbon in a protected or a reducing atmosphere, e.g. carbides of Groups II-A, III-A and IV-A.

The reaction of the metal with a carburizing gas, i.e. heating the metal in the vapour of a suitable hydrocarbon, e.g. carbides of Groups VIII and I-B.

Precipitation from the gas phase (acetylene) by reacting the metal halide/carbonyl in hydrogen or with metal organic compounds, e.g. carbides of Group II-B.

In addition, the present work gives an additional and useful method, namely ion bombardment of the metals in a carbon-containing atmosphere, for preparing a great variety of carbides, particularly unstable ones. This could further be supported by other experimental observations, namely the bombardment of some metals with rare-gas ions in an O_2 , N_2 or H_2 atmosphere where carbon contamination promotes the incorporation of gases in the surface layers of the metals [1-5].

The stability of transition metal carbides decreases on going from left to right across the periodic table. Thus, TiC is highly stable, while Fe_3C and Ni_3C are least stable (see Table 1). The influence of such an effect is clearly seen from the enhanced intensity of the carbide peaks on TiFe (Fig. 2). This result certainly shows that the reaction products are controlled mainly by thermodynamic factors. The chemical reaction and the effect of the incident beam will become significant only when the formation of the carbide is strongly favoured. Hence, the role of the bombarding gas is largely to provide a mechanism for the equilibrium of the surface components. However, one cannot rule out the possibility of producing thermodynamically unfavourable compounds, such as those observed in this study, under the present experimental conditions. In other words, they may be formed through some intermediate forms under the influence of the ion bombardment.

Even though carbide formation is essentially based on the chemical reactivity of metal with carbon, it also depends on the crystal structure of the surface, the surface roughness, etc. With regard to the physical process, the promotion of carbide formation by argon ion bombardment can be primarily attributed to knock-on collisions by argon ions at the surface. However, the contribution of the chemical reaction must be considered in order to interpret the large difference in the reaction rate of carbide formation between various metals [3-5]. Hence, it is not clear whether the overall process is thermodynamic or kinetic in origin or whether it is governed by a simultaneous process. However, based on the foregoing arguments, it could be suggested that the formation of

surface carbides by argon ion bombardment occurs through a thermochemical reaction assisted by physical processes such as knock-on collisions.

We have found, without exception, that a correlation exists between the reactivity of the carbide and the observed XPS signals. For example, in the case of Mg_2Cu the peak due to the carbide is shallower than the peak due to Mg_2Ni where a relatively sharp feature appears. This could even be seen with Mg_2NiH_4 (see Figs. 2 and 3). For Mg_2Cu the contribution to the carbide due to Cu is probably small or even negligible. This could be supported by the fact that putative Cu carbide (Cu_3C) is less stable than Fe_3C and Ni_3C , as judged by their strength of bonding [28]. Accordingly, the carbides show a marked decrease in stability on going from Fe to Ni to Cu. Many of these compounds are not fully characterized. This is mainly due to experimental difficulties and the lack of interest in the past. So far, the deposition of carbon on a metal surface has been studied extensively for the intermediates for catalytic hydrocarbon synthesis, gasification of carbon and catalyst poisons [29–32]. The high selectivity with which Cu converts the synthesis gas to methanol, rather than hydrocarbons, reflects their inability to form surface carbides or to dissociate CO. In other words, the carbidic carbon is unstable on the Cu surface with respect to a graphite layer. In the case of Fe and Ni surfaces a carbide-like species, albeit of low stability and very labile, is found to be always present on the active catalyst following the reaction and is identified as a precursor to methane formation.

Although the present data are not extensive enough to permit an accurate determination of the relative importance of ion bombardment vs. composition, the influence of the former is evident. Nevertheless, for given vacuum conditions carbide formation can be eliminated or reduced by choosing the right sputter conditions. Before examining this point, it is necessary to describe the various ion-induced processes and the consequences in order to obtain a better understanding of the different phenomena that occur at the surface. Upon sputtering, the bombarding ion penetrates the solid to a certain depth and transfers its kinetic energy to the lattice. Some of the energy transferred to the lattice may reach the surface through consecutive impacts and may be transmitted to a single surface atom or to clusters of atoms. If this energy exceeds the binding energy, neutral or charged atoms or molecules may be emitted. As the ion bombardment progresses, the surface is removed by sputtering and the lower layers are uncovered by impurities for analysis. The energy received by lattice atoms inside and at the surface of the body may exceed the binding energies in molecules by several orders of magnitude. It thus suffices to break chemical bonds and to form new ones. New compounds are most likely to arise through the formation and reorganization of fragment molecules or disturbed lattice zones, but they may also be formed through reactions of isolated particles with each other and with neighbouring molecules. Accordingly, the carbide layers are produced by the combined effect of ion bombardment and carbon

contamination. The formation of such surface carbide species can affect depth profile analysis in several ways [1–8]. For example:

- at low sputter rates, an apparent concentration-depth profile for carbon may be observed which, however, does not correspond to the reality;
- carbide formation can also alter the relative amplitudes and position of the ligand and metal peaks, and this interferes with the determination of the stoichiometry;
- it is likely that the carbide formation negatively influences depth resolution because carbides are difficult to sputter.

Even though the characterization of surfaces has been performed under UHV conditions, carbon from contamination serves as a main source for carbide formation. Such contamination layers on the samples were produced by any or all of the following [1–8, 33].

- Mere exposure of a sample to air for short periods of time permits surface adsorption of atmospheric gases; in particular, carbon-containing gases are important in the present context.
- At pressures of 10^{-6} mbar (a typical condition for argon ion bombardment), a clean surface would be completely covered by an adsorbed monolayer of the background gas in a period of about 1 s.
- Since ion pumps are usually shut off at the time of sputtering, it is possible that during prolonged depth profile analysis impurities can build up to partial pressures close to the critical limit. In other words, the rate of adsorption of impurities could be greater than the removal rate of the adsorbed species.
- Once the sample is placed in the spectrometer, sufficient back-diffusion of pump oil into the sample chamber through the vacuum system can deposit thin layers of carbon onto the sample.
- A further source of carbon is the contamination from residual gases in the spectrometer owing to poor vacuum conditions.

Therefore, we suggest the following points to reduce or remove carbide formation during cleaning of the surface and/or depth profile analysis. However, we will not speculate on the details of the mechanism for carbide formation except to emphasize a few important properties and methods for the elimination of such surface contamination, based on literature reports [1–8, 33] and substantially from our own findings.

- The vacuum system should be evacuated to about 10^{-10} mbar. High purity argon is then leaked in to allow for sputtering at a pressure of typically 5×10^{-6} mbar.
- The sputtering gas purity required should meet the partial pressure of 2×10^{-8} mbar.
- It is necessary to work at a high ion current density to keep the partial pressure of carbon compounds to the lowest possible. Typical conditions are $i_{\text{ion}}/P_i > 10^8$, with an ion current density (i_{ion}) in $\mu\text{A cm}^{-2}$ and the partial pressure

(P_i) of impurities in Torr (1 Torr = 1.333 mbar), i.e. high sputter rates are desirable to minimize carbon adsorption.

– As the contamination layers were produced by exposure of the samples to air for a short while, the time exposure should, of course, be minimized.

– The sample should be transferred to the analysis chamber under an argon atmosphere without contacting air. Thus, the amount of trace contamination is decreased significantly.

– To avoid an increase of monolayer contaminants for a typical measurement time (about 100 s), it is necessary to work at low impurity base pressure (below 10^{-10} mbar).

– To eliminate pump oil deposition, a metallic screen may be placed close to the sample between it and the vacuum port within the compartment. The screen is cooled to liquid N_2 temperature, effectively freezing out any contaminants, such as pump oil, that diffuse into the chamber.

– To reduce further contamination, a Ti sublimation pump with a cryopanel usually serves as an efficient scavenger for the reactive gases.

– Instead of “static” systems, by using a more modern type of ion gun operating in a “dynamic” mode with constant throughput of the sputtering gas (pumped away by the main chamber pump), the overall contamination is decreased.

– An additional improvement is differential pumping of the ion gun by a getter pump or by an added turbomolecular or diffusion pump.

In conclusion, the effects described here may have important applications. For example, there may be a severe limitation on the use of certain materials in radiation environments, particularly if the compounds are being used in their traditional role as insulators or catalysts. However, by optimizing the vacuum and sputtering conditions as well as by adopting an appropriate sample handling technique, the formation of undesired surface carbides upon ion bombardment could be avoided completely or reduced to a reasonable level. Although the problem of the effect of ion bombardment on the properties of materials is relatively new, the existence of ion-induced reactions (and several others) is undisputed [1–8]. However, this does not mean that the phenomena discussed above have been studied well and fully enough. Apparently, most of the studies along this line still lie in the future. The results of the experiments discussed in this study show that by ion bombardment one can not only alter the parameters of materials in a controlled way, but one can also obtain materials with properties that cannot be obtained using other technological means. Consequently, along with solving varied applied problems, studies in this direction should facilitate the development of solid state and surface chemistry and physics of materials.

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