GAS PHASE RECOMBINATION OF IONIC MOLECULES FOR ION-INDUCED SURFACE EMISSION

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The gas phase recombination mechanism has been used to interpret ion-induced emission from $TiSi_2$ and $MoSi_2$ surfaces in the presence of Cl_2 . Direct time-of-flight measurements have been performed on Si⁺, SiCl⁺, Ti⁺ and TiCl⁺ emitted from $TiSi_2$ and on Si⁺, SiCl⁺, Mo⁺ and MoCl⁺ emitted from $MoSi_2$. It was found that the ionic molecular products were formed by recombination above the surface of a neutral Cl atom and an ionized metal or semiconductor atom. Theoretical calculations based on this approach agree very well with experimental data down to about 1 eV when an image potential adjustment is considered. This accounts for over 90% of the emitted ionic molecular products. It is significant that the emission of $SiCl^+$ from $TiSi_2$ and $MoSi_2$ results from a different mechanism than emission of neutral SiCl from elemental Si.

1. Introduction

The mechanisms of molecular ejection from surfaces due to energetic ion stimulation have been the focus of particular research interest during the past -8,11,12,15]. A variety of mechanisms have been used to explain few yea. various ion-induced emission phenomena. The range of these phenomena depends primarily on the emission parameters such as molecular binding energies, incident ion energies, effects of adsorbed reactive gases, and the occurrence of altered surfaces. These different mechanisms can be described in terms of two general processes, physical and thermal. Thermal processes are usually associated with emission of a volatile molecular species where the incident ion aids in the formation of the volatile species, usually consisting of one or more surface atom(s) and adsorbed reactive gas atom(s). The compounds thus formed usually leave the surface with an equilibrium temperature somewhat higher than the ambient temperature due to the surface heating associated with impact from the incident ions. For the thermal process, the ion participates in the reaction both by aiding in the formation of the emitted molecule and by increasing the local temperature of the surface.

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In the physical process, material is emitted from the surface by momentum transfer from the incident ion. For molecular species, this can occur in general by two possible mechanisms, direct emission or recombination. The collisional-cascade model has been used to describe the direct molecular emission by assuming that the molecular acts as a hard sphere [1]. In this model, the incident ion causes a binary collisional-cascade near the surface. Atoms, or molecules treated in the hard sphere approximation, near the surface will be emitted if they receive enough energy to overcome the surface binding energy. On the other hand, recombination to form molecular species occurs when two or more atoms emitted separately during a collisional-cascade combine above the surface [2]. The dissociation energy of the molecule is the important parameter in this model since recombination occurs only when the atoms' relative kinetic energy is less than the molecular dissociation energy of the product. The recombination mechanism does not preclude the prior existence of the molecules on the surface, but suggests that the individual atoms in the molecule are emitted independently rather than as a unit.

Silicon is probably the most widely studied substrate in ion-induced molecular emission. In the silicon etching experiments, which are particularly important to the understanding of reactive ion etching, inert ions strike the surface in the presence of reactive gases such as XeF₂ or Cl₂. Dieleman and coworkers [3,15] studied the products of Si in a Cl₂ environment and found that a combination of thermal and physical mechanisms were applicable. The relative abundance of the various emission products due to the two mechanisms depends on the incident ion energy and on the incident flux ratio of Cl, to Ar⁺. Haring et al. have published detailed studies of ion-induced emission of the neutral parent(s) of SiF_3^+ from Si in an XeF₂ environment [5]. Haring et al. [5] have determined that this process proceeds by a direct collisional-cascade mechanism. More recently however, Houle [6] has cautioned against interpreting data completely in the manner of Haring et al. [5] and suggests that the same data could be used to support the occurrence of thermal emission [6]. The recombination theory of Konnen et al. [2] has been used to explain emission of noble gas clusters [7], K₂ emission from polycrystalline K [2] and KI emission from solid KI₂ [2].

In order to clarify our understanding on the applicability of the different emission mechanisms, we studied in detail the ion-induced emission of SiCl⁺ and TiCl⁺ from TiSi₂ and the emission of SiCl⁺ and MoCl⁺ from MoSi₂. Experimental data are compared here both to the thermal mechanism and the two physical mechanisms referred to above. We have found that, in each case, the product waveforms follow most closely the form predicted by the recombination model on the assumption that neutral chlorine combines with ionic metal atoms or ionic semiconductor atoms above the surface. We rule out the possibility of Cl⁺ combining with neutral Si, Ti or Mo since we observe no Cl⁺ emission from these surfaces. Our measurements differ from those mentioned in the preceding overview in that we measure ionic products rather than neutral products.

2. Experimental apparatus and measurements

The experimental apparatus and measurement procedure have been described in detail previously [8]. In short, a 4 microsecond, 500 eV (0.2 mA/cm^2) Ar^+ pulse strikes the substrate which is simultaneously exposed to 1×10^{-5} Torr Cl₂. A quadrupole mass analyzer (QMA) (with the ionizer off) measures the mass selected ionized product waveform using pulse counting techniques. The repetition rate of the ion pulse is on the order of 500 Hz and data are collected over a period of approximately 30 min. The entire time-of-flight measurement is performed in a stainless steel ultra high vacuum chamber with a base pressure of 2×10^{-10} Torr and surface probes for characterizing the sample surface. See fig. 1 for the general arrangement.

3. The recombination model

The recombination model for diatomic molecules emitted from surfaces has been explicitly presented by Konnen et al. [2]. In this model, two nearest neighbor atoms are independently and simultaneously emitted from the surface during a collisional-cascade process initiated by the incident ion. If at the outset of emission, the relative kinetic energy, ϵ , of the two atoms is less than their molecular potential energy a molecule will form. The recombination



Fig. 1. Ultra high vacuum system in time-of-flight configuration with sample, TiSi₂ or MoSi₂, in focal point of pulsed ion gun, chlorine doser, and quadrupole mass analyzer (QMA).

model gives the normalized momentum distribution w(P) of a diatomic molecule formed by the recombination of atoms 1 and 2 as:

$$w(\boldsymbol{P}) = \int_0^{\sqrt{2\mu E_d}} \mathrm{d}\xi \ \xi^2 \int \mathrm{d}\boldsymbol{u} \ \Phi_1(q_1 \boldsymbol{P} + \boldsymbol{\xi} \boldsymbol{u}) \ \Phi_2(q_2 \boldsymbol{P} - \boldsymbol{\xi} \boldsymbol{u}),$$

where ξ is $(2\mu\epsilon)^{1/2}$, E_d is the molecular dissociation energy, $q_i = m_i/M$ with M being $m_1 + m_2$, μ is the reduced mass of atoms 1 and 2, u is the unit vector in the direction of the relative momentum of atoms 1 and 2, and $\Phi_1(q_1P + \xi u)$ and $\Phi_2(q_2P - \xi u)$ are the emitted fluxes of the two independently emitted atoms. In general the emitted molecule will have excess internal energy due to the nonzero ϵ and the fact that the nearest neighbor distance on the surface will not generally be equal to the bond length of the molecule, see fig. 2. Due



Fig. 2. Molecular potential energy diagram of atoms on surface (bottom), and of molecule in gas phase (top). Actual potential energy of the two atoms varies continuously between these during emission. Immediately after emission the two atom system contains relative kinetic energy ϵ . If throughout emission $V + \epsilon < 0$ the atoms will form a molecule, V being the atoms' relative potential energy. This molecule will typically be in some excited state. Konnen assumes in his recombination model that the molecule will form if $\epsilon < E_d$, E_d being the molecular dissociation energy.



Fig. 3. Time-of-flight measurements of Ti⁺ from TiSi₂ and Mo⁺ from MoSi₂. These distributions are used in eq. (1) after being adjusted by an image potential.



Fig. 4. Energy level diagram describing effects of image potential on recombination model. Top: neutral Cl is emitted by collisional-cascade mechanism with surface binding energy U_{Cl} . Bottom: Si⁺ is emitted and must overcome both the surface binding energy, U_{Si} , and its image potential, the measured kinetic energy is $E(Si^+)$. Middle: recombination occurs near the surface where SiCl⁺ is effected by its image potential, the measured kinetic energy is $E(SiCl^+)$.

to the low probability of collisions at the pressures used the molecule will remain in this excited state after it leaves the surface.

We have previously reported the Si⁺ emission distribution from TiSi₂ and MoSi₂ [8] and have also measured the Ti⁺ and Mo⁺ emission from their respective silicides (fig. 3). The velocity fluxes calculated [8] from these TOF measurements can be directly inserted into eq. (1). The flux of the emitted chlorine neutral has been assumed to be defined in terms of the collisional-cascade mechanism. The collisional-cascade model has a single free parameter, the surface binding energy, U, and an emitted energy flux proportional to $E/(U+E)^3$, where E is the kinetic energy. This leaves two unknowns in eq. (1), E_d and U_{Cl} . Since we detect ions as products, an image potential adjustment must also be applied to the emitted flux. An energy diagram for Cl, Si⁺ and SiCl⁺ emission is shown in fig. 4. Discussion of this diagram is contained in section 6.

4. Results for SiCl + emission

Before examining the SiCl⁺ results in terms of the recombination theory, we first determined the value of E_d for SiCl⁺. This was accomplished using the following cyclic thermodynamic processes,

SiCl
$$\xrightarrow{E_{dSiCl}}$$
 Si + Cl
 I_{SiCl} I_{Si}
SiCl + $e^{-\frac{E_{dSiCl}}{+}}$ Si + Cl + $e^{-\frac{E$

where I is an ionization potential. Using values of E_d for SiCl = 4.5 eV [9] $I_{si} = 8.15 \text{ eV}$ [9] and $I_{SiCl} = 7.4 \text{ eV}$ [10], E_d of SiCl⁺ is determined to be 5.3 eV. With this value of E_d the SiCl⁺ time-of-flight data was fitted by varying both U_{Cl} and the image potential, V_{im} . The best fit found for SiCl⁺ emission from TiSi₂ is shown in fig. 5, with $U_{Cl} = 1.3 \text{ eV}$ and $V_{im} = 1.4 \text{ eV}$. The model compares very favorably with the data down to about 1 eV. Also shown in fig. 5 is the same theoretical fit without the image potential correction showing the importance of that contribution.

In fig. 6 we compare the experimental data with the thermal emission mechanism, using a temperature of 450 K. A temperature value of 450 K was chosen based on the observations of Rossen and Sawin [11] and our own unpublished data for neutral SiCl emission from Si under similar conditions. In both Rossen and Sawin's experiments and ours, the SiCl neutral product distributions could be satisfactorily interpreted in terms of thermal desorption



Fig. 5. Theoretical fit of experimental spectra for SiCl⁺ emitted from TiSi₂ surface, solid line. Same fit without image potential adjustment, dashed line. Inset shows corresponding energy distributions.



Fig. 6. Comparison of same experimental spectra in fig. 5 to the hard sphere collisional-cascade model (CC), and the thermal desorption model (TD). Choice of parameters for each model is outlined in the text.

with an equilibrium temperature of 450 K. In fig. 6 the experimental data is also compared to the direct emission collisional-cascade model in which the surface binding energy U has been taken as 0.3 eV. This value of U was found by Kolfschoten et al. [12] by fitting the low and intermediate energy portions for neutral SiCl emission from Si. The collisional-cascade direct emission model was adjusted for ionization probability [14], and both the direct emission and the thermal emission models were adjusted for image potential effects [13]. The values of the parameters used for the two mechanisms in fig. 5 are from a different experiment, SiCl emitted from Si, not SiCl⁺ emitted from TiSi₂. These values were chosen for illustration since no reasonable fit could be obtained by varying the parameter values. Clearly the recombination model provides the better interpretation of the experimental data. For SiCl⁺ from MoSi₂, values of $U_{Cl} = 1.2$ eV and $V_{im} = 1.2$ eV were found. This fit was also good down to about 1 eV.

5. Results for TiCi + and MoCl + emission

For TiCl⁺ and MoCl⁺ molecules emitted from their respective silicides values of E_d could not be determined from the thermodynamic cyclic process, since I_{MoCl} , I_{TiCl} and E_d for MoCl are not known. Values of U_{Cl} have been



Fig. 7. Theoretical best fits and experimental data for M₀Cl⁺ emission from MoSi₂ and TiCl⁺ emission from TiSi₂

determined for the two silicides surfaces from the SiCl⁺ comparisons above, so by varying E_d and V_{im} a least-squares fit could be obtained for the metal chloride ions. The data and the recombination model comparisons are shown in fig. 7. For TiCl⁺ emission from TiSi₂, $E_d = 4.5$ eV and $V_{im} = 1.3$ eV. For MoCl⁺ emission from MoSi₂, $E_d = 4.0$ eV and $V_{im} = 2.0$ eV. Using the experimentally obtained value of E_d for TiCl⁺ and the values $I_{Ti} = 6.8$ eV [9] and E_d for TiCl = 4.9 eV [9] we determine a value for $I_{TiCl} = 7.2$ eV from the above thermodynamic cycle. An experimental value for the ionization potential of MoCl could not be determined since E_d for MoCl is not available.

6. Discussion

To achieve an improved understanding of the mechanisms of emission for these molecular ions, it is instructive to view the process as it proceeds slowly in terms of the recombination model and paying close attention to the effects of the image potential. As stated above, the recombination model does not preclude the existence of the molecule on the surface. In fact the restriction that E_d be greater than the atoms' relative kinetic energy implies that atoms forming the molecule must be nearest neighbors on the surface [2]. Existing in such proximity, the two atoms which will eventually form the detected molecule can be characterized by a pairwise interaction prior to emission. This can range between a weak interaction to a chemical bond or can be essentially metallic in nature. In direct physical sputtering, this interaction within the surface molecule is assumed to be infinitely strong, thus the hard molecule is emitted in the same fashion as an atom. The recombination model makes no direct use of this interaction; it assumes that the atoms which will eventually form the molecule are emitted independently and form the molecule only if E_{d} is greater than the atoms' relative kinetic energy. The final state of emission for the two atoms is a bound state, the atoms leave the surface as a molecule.

As ions leave the surface, some of their kinetic energy is used to overcome an image potential. In treating our data, we have assumed that the image potential acts solely on the molecules, $SiCl^+$, $TiCl^+$ and $MoCl^+$. Since recombination occurs close to the surface, we have ignored any image potential effect on the sputtered ions, Si^+ , Ti^+ and Mo^+ before they combine to form the molecules. On this assumption, the measured distributions of Si^+ , Ti^+ and Mo^+ were adjusted for their image potentials before they were introduced into eq. (1) [8,13]. This adjustment gives the velocity distribution near the surface which is relevant to the recombination model.

In fig. 4 we detail the mechanism discussed above in terms of energy. The emitted neutral chlorine flux is determined by the value of U_{Cl} from the collisional-cascade model [1]. The measured emitted flux of Si⁺ is determined by both its surface bonding energy, U_{Si} , and image potential. The values

 $E(SiCl^+)$ and $E(Si^+)$ are the energies determined from the time-of-flight measurements. If recombination occurs and the product is an ion, the kinetic energy of the product is reduced by the image potential before it is detected. In fig. 4 it can be seen why the measured distributions of Si⁺, Ti⁺ and Mo⁺ were adjusted by their image potentials to correspond to their fluxes close to the surface where recombination occurs. A value of 1.4 eV for the image potential was assumed for the Si⁺, Ti⁺ and Mo⁺ spectra [8].

In a more complete recombination theory for ionic species, the ionization probability (flux of ions/flux of neutrals) must be considered for both atomic species before recombination occurs as well as for the specific molecular species [14]. Surface ionization for the atomic products Si^+ , Ti^+ and Mo^+ from these silicide surfaces has been explained in terms of the electron tunneling model [8]. In this model [14], ions are emitted from the surface. As the ion leaves the surface, its ionization level is lowered below the Fermi level of the substrate. When the energy levels cross, an electron can tunnel from the substrate to the ion, neutralizing the ion. The slower the ion is traveling, the more time it spends near a favorable tunneling region, and therefore the greater chance it has of being neutralized [14].

Exact incorporation of the ionization probability theory would be difficult since, for one reason, the ionization probability depends on the emitted species ionization potential. The ionization potential of the emitted molecules will depend on their excess internal energy and how it is partitioned. For ease of calculation, we assume all the surface ionization processes to be contained in the measured Si⁺, Ti⁺ or Mo⁺ distributions [8]. This assumption could explain the deviations observed at low energies as indicated in fig. 5 and fig. 7, since the ionization probability goes to zero at low energies [14].

The model as stated above can be outlined in terms of the following stepwise mechanism for the recombination of $SiCl^+$ above the $TiSi_2$ surface in the presence of Cl_2 :

(1) Neutral Cl and Si⁺ are simultaneously emitted into a bound state when an incident argon ion strikes the surface.

(2) The $SiCl^+$ has a velocity dependent probability of being neutralized through electron tunneling from the surface as it leaves the surface region.

(3) As the SiCl⁺ leaves the surface region it is slowed by an energy equal to its image potential.

The same general sequence holds for TiCl⁺ emission from TiSi₂ and for SiCl⁺ and MoCl⁺ emission from MoSi₂.

As stated in the introduction, ion-induced SiCl emission from Si has been interpreted in terms of thermal desorption [3,11] or the direct emission collisional-cascade model [3,15]. The difference in our studies and previous work is due either to the difference in the products (neutral versus ionic) and/or the difference in the surfaces. The dissociation energy of SiCl⁺ is greater than the dissociation energy of SiCl (above). This suggests that

recombination would be more prevalent for SiCl⁺ emission than for SiCl emission. In an experiment similiar to that of Rossen ard Sawin [11], we have detected neutral SiCl emitted from both TiSi_2 and Si(111). From the Si(111) surface we found that neutral SiCl was emitted primarily by a thermal desorption mechanism with an equilibrium temperature of 450 K. On the other hand, neutral SiCl emitted from the TiSi_2 surface showed both thermal and physical emission characteristics. The results of these experiments provide only preliminary information, but they clearly indicate that the surface plays an important role in the determination of the emission mechanism.

To check the validity of the above model in a more conclusive way, something should be said of the experimentally derived values of $V_{\rm im}$, $I_{\rm Cl}$ and $I_{\rm TiCl}$. The image potential corrections found are not unreasonable based on previous work of atomic ion emission [8,13]. A value of $U_{\rm Cl}$ has been reported for Cl on elemental Si for these types of experiments [15]. Unfortunately this value was reported as a "few eV" due to some experimental difficulties [15]. This is consistent with the value of 1.4 eV found for $U_{\rm Cl}$. As stated above no experimental or theoretical value for $I_{\rm TiCl}$ is available for comparison.

7. Conclusion

It has been shown that the ionic molecular products SiCl⁺, TiCl⁺ and MoCl⁺ emitted from TiSi₂ and MoSi₂ surfaces respectively follow the recombination model down to 1 eV in product energy. This includes well over 90% of the detected ionic molecular products. The diatomic ionic molecules TiCl⁺, MoCl⁺ and SiCl⁺ are formed when neutral Cl emitted from the surface combines with either Ti⁺, Mo⁺ or Si⁺ respectively. A critical comparison using the recombination model was made using an experimentally measured flux for the ionic species and a collisional-cascade derived flux for the neutral chlorine. The ion-induced SiCl⁺ emission from these silicide surfaces clearly follows a mechanism different from that for neutral SiCl emission from Si. The difference can be attributed to the ionic nature of the product and/or the different surfaces. The recombination model does not preclude the existence of the detected molecule on the surface but suggests that the chemical bond of the gas phase product evolves from an interaction between the constituent atoms on the surface. An experimental value for the ionization potential of TiCl was obtained indirectly by fitting the data and making a thermodynamic cycle calculation.

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