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Mechanism of the ion dimer formation in secondary ion mass spectrometry

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Abstract

The influence of temperature on the emission of the Ni_2^+ and Ni^+ secondary ions has been investigated in the temperature range from 350 to 1100 K using secondary ion mass spectrometry. The ferroparamagnetic phase transition at $T \cong 620$ K on nickel is found to strongly affect only the emission of Ni^+ but not the emission of Ni_2^+. The data show that the Ni_2^+ dimers form via the ion–molecule recombination reaction in the near surface region rather than by a direct emission of the bound molecules. (Int J Mass Spectrom 188 (1999) 183–187) © 1999 Elsevier Science B.V.

Keywords: SIMS; Nickel; Sputtering; Ion emission; Ion dimer

1. Introduction

The investigation of processes of the interaction of an ion beam with the metal surfaces at different temperatures provides the unique possibility to study magnetic materials since the surface binding energies, interatom interaction potentials, surface relaxation, etc. can change drastically near the Curie point (T_C). (See reviews in [1,2].)

In general, two basic mechanisms of the formation of positively charged clusters are distinguished—recombination and fragmentation. In the latter mechanism, the sputtered clusters leave the surface as an entity, that is, the constituents were nearest neighbours and were bound before the ejection event, whereas in the recombination scheme, the neutral atoms and the ion species, which are to constitute the clusters, leave the surface independently. The specific excitation mechanisms are usually thought to play a negligible role and in most cases are not considered. It is generally accepted that the positive ions form via the recombination mechanism, and the oxide ions and the negatively charged ions form via the fragmentation mechanism [3–7]. In particular, classical dynamics calculations [3–5] indicate that Ni_2^+ ions form over the surface via interaction between Ni^+ ions and Ni atoms. However, the data obtained for Al_n^+ and Si_n^+ contradict the long-standing conviction that the emission of positive secondary ions is best described within the framework of the recombination mechanism [8]. It suffices to mention that the presently available data from experiments and computer simulations are not conclusive with respect to what mechanism is the dominant one [9]. We suppose, that the temperature investigations of secondary ion emission

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in the phase transition region could be highly informative and may shed light on the mechanism of the cluster formation.

In this article, the influence of the temperature on the emission of Ni^+ and Ni_2^+ secondary ions has been investigated using 3 keV Ar^+ and Xe^+ ion bombardment of polycrystalline nickel. In discussing the effect of the magnetic phase transition at $T \cong 620$ K on the secondary ion emission, we mainly aim at determination of the mechanism of the ion dimer formation. The results show that the recombination mechanism in Ni_2^+ dimer formation is predominant.

2. Experimental

The experiments were carried out using a conventional VHV secondary ion mass spectrometry (SIMS) instrument described in detail elsewhere [10]. The sample was bombarded by 3 keV Ar^+ and Xe^+ ions, at incident angle 45 °, the beam current, J, was ~0.7 μA over an area of about 0.05 cm^2. The secondary ions were collected in the energy range 0–10 eV, so that the major part of the ions were registered [9]. The pressure of residual gases in the mass spectrometer chamber did not exceed $P = 7 \times 10^{-7}$ Pa, thus providing the experimental conditions of a dynamically clean surface, $P(\mathrm{Pa}) \ll 10^{-6}\ J(\mu\mathrm{A/cm}^2)$ [11].

Ar and Xe gases (99.998%) were additionally purified by filtering through zeolite. The polycrystalline Ni foil (99.99%) of 0.1 mm thickness was treated before each experiment by annealing in vacuum at 1100 K for 40 min and subsequent ion sputtering for 60 min.

The temperature was determined using a W(5%)Re–W(20%)Re thermocouple spot-welded to the sample back. The sample was automatically linearly heated (or cooled) from 350 to 1100 K with accuracy of 2 K. The rate of heating (or cooling) of sample was varied from 10 to 70 K/min. Each run was repeated eight times.

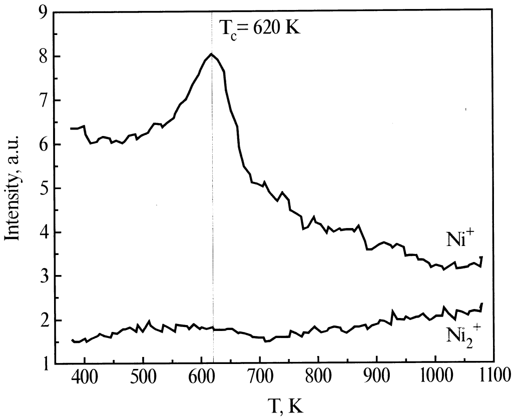

Fig. 1. Temperature dependence of the Ni^+ and Ni_2^+ intensities during Xe^+ ion bombardment of nickel foil.

3. Results and discussion

Fig. 1 shows the Ni^+ and Ni_2^+ ion intensities as a function of temperature during bombardment of Ni foil by Xe^+. The identical results were obtained using Ar^+ beam, therefore, only the curves for the case of Xe^+ bombardment will be shown throughout. One can see an increase in the Ni^+ intensity near 620 K, although this is not observed for the Ni_2^+ intensity. This fact is clearly reflected in Fig. 2, which depicts the dependence of $\ln(Ni_2^+/Ni^+)$ on the inverse sample temperature.

Obviously, the effect of the Ni^+ intensity increase in the range from 500 to 620 K is accounted for by the

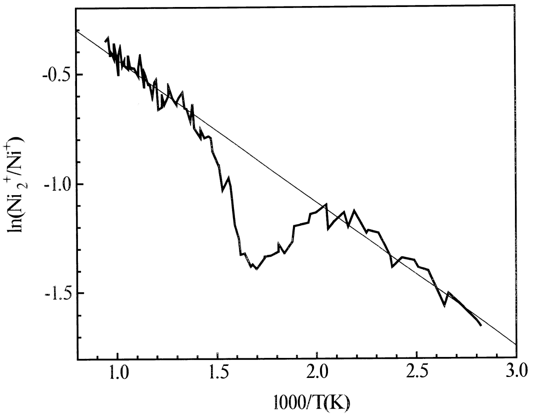

Fig. 2. Plot of $\ln(Ni_2^+/Ni^+)$ vs. inverse absolute temperature.

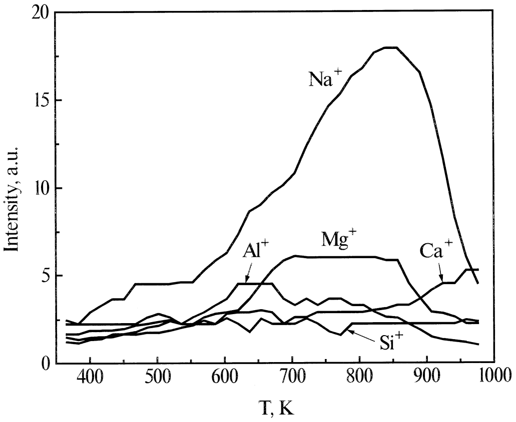

Fig. 3. Temperature dependence of the impurity intensities during Xe$^+$ ion bombardment of nickel foil.

magnetic phase transition. This phenomenon is well known [1,2] and the spike of the Ni$^+$ intensity in the phase transition region appears to be the result of both the sputter yield rise and the ionisation probability increase [Eqs. (1) and (2)]. Indeed, a 0.06–0.08 eV decrease in work function occurs at transition from ferro- to paramagnetic phase [12,13]. In addition, an increase in sputter yield for polycrystalline Ni near T_C was experimentally found to be about 10% [2]. Recently, theoretical explanation of this effect was suggested [14].

It must be noted that the interpretation of results of the SIMS experimental studies aimed at the investigation of temperature dependence of the secondary ion emission can be complicated by a significant influence of impurities on the ion emission. Thus, it is important that the sample and the gases used for bombardment be of high purity and the conditions of dynamically clean surface be fulfilled. The temperature dependence of the intensities of impurity ions are shown in Fig. 3. One can see that there is no correlation between the Ni$^+$ intensity and the impurity intensities. In particular, the Na and Mg impurities are not responsible for the Ni$^+$ intensity decrease and the Ni$_2^+$ intensity growth at $T > 700$ K since the Na$^+$ and Mg$^+$ intensities fall at $T > 850$ K, which is not observed for the Ni$^+$ and Ni$_2^+$ intensities.

It is well known that the intensity of atomic ions can be described as follows:

$$I = AJCSP^+ \tag{1}$$

where A is a constant, J is the primary ion density, C is the concentration, S is the sputter yield, and P^+ is the ionisation probability. The temperature is known to have only a weak influence, if any, on the sputter yield [15,16]. The electron tunneling model has proved to fairly well describe the ionisation process of the particles sputtered from metal surfaces [17–20]. According to this model:

$$P^+ \cong \exp[-(I_i - \phi)/\epsilon] \tag{2}$$

where I_i is the ionisation energy of sputtered molecules or atoms, ϕ is the work function, and ϵ is the velocity constant. Obviously, this description of the intensity of atomic ions by Eqs. (1) and (2) is valid as well for the molecular ions, which form via the fragmentation mechanism. Since the work function is weakly dependent on temperature, $\alpha = d\phi/dT$ is of the order of Boltzmann's constant [21], the influence of temperature on the ionisation probability is negligible. In addition, the model of ionisation process for nonzero temperatures [22] predicts the temperature term of the ionisation probability, as we have estimated, to be insignificant. Finally, in the case of fragmentation mechanism, the Ni$_2^+$ and Ni$^+$ intensity ratio should not depend on the target temperature.

At temperatures higher than 650 K and lower than 500 K, the Ni$^+$ intensity is seen to decline, while the Ni$_2^+$ intensity slightly increases (Fig. 1). We believe that the decrease in the Ni$^+$ intensity and the increase in the Ni$_2^+$ intensity result from an ion–molecule reaction occurring in the near surface region. The scheme of this reaction can be denoted as follows:

$$\mathrm{Ni}^+ + [\mathrm{Ni}_n]^* \rightleftarrows \mathrm{Ni}_2^+ + [\mathrm{Ni}_{n-1}]^* \tag{3}$$

where $[\mathrm{Ni}_n]^*$ and $[\mathrm{Ni}_{n-1}]^*$ are the excited fragments of (n) and ($n - 1$) atoms, respectively, produced by ion bombardment. The slight rise in the Ni$_2^+$ dimer intensity with temperature may be due to an increase in reaction rate or to a shift of reaction equilibrium. The curve of Fig. 2 is well approximated by a linear regression just except for the anomalous region near T_C. This implies that the ion–molecule reaction (3) occurs under the thermodynamic equilibrium condition. Therefore, the fact of the temperature curve of Ni_2^+/Ni^+ ratio not being approximated by the linear regression near T_C is probably due to the fact that thermodynamic equilibrium is not established during the phase transition of second type [23,24]. In summary, the Ni_2^+ dimers are likely to form via the ion–molecule reaction occurring in the surface region, that is, via the recombination mechanism. Note that the possible influence of the species such as Ni_3^+, Ni_4^+, Ni_5^+, etc. on the Ni^+ and Ni_2^+ intensities is negligible since their intensities are a few orders of magnitude less than the Ni^+ and Ni_2^+ intensities [8].

If thermodynamic equilibrium is assumed, one can write

$$K \propto \frac{I_{Ni_2^+}}{I_{Ni^+}}$$

where K is the equilibrium constant, $I_{Ni_2^+}$ and I_{Ni^+} are the intensities of the Ni_2^+ and Ni^+ ions, respectively.

Taking into account that the equilibrium constant is proportional to $\exp(-\Delta G/kT)$, we obtain

$$I_{Ni_2^+} \propto e^{-\Delta G/kT} I_{Ni^+}$$

where ΔG is the change in Gibbs free energy. The values of ΔG have been found to be equal to 0.061 ± 0.009 and 0.056 ± 0.007 eV for the cases of Ar^+ and Xe^+ bombardment, respectively.

The energy levels for initial and final products of the reaction (3) can be written as (atom energy in the bulk of metal accepted for zero)

initial:

$$IP(Ni^+) + E_s(Ni) + nE_s(Ni) - \Delta(Ni_n)$$

final:

$$IP(Ni_2^+) + 2E_s(Ni) - D(Ni^+–Ni) + (n-1)E_s(Ni) - \Delta(Ni_{n-1})$$

where $IP(Ni^+)$, $IP(Ni_2^+)$ are the ionisation potentials of Ni and Ni_2. $IP(Ni^+) = IP(Ni_2^+) = 7.63$ eV [25], $E_s(Ni)$ is the sublimation energy for nickel atom, $D(Ni^+–Ni)$ is the dissociation energy for Ni_2^+ ion: $D(Ni^+–Ni) = 2.08$ eV [25,26], $\Delta(Ni_n)$, $\Delta(Ni_{n-1})$ are the total binding energies of nickel atoms in clusters consisting of n and $n-1$ atoms [reaction (3)].

Table 1
Calculated values of ΔH

n	ΔH (eV)
1	−2.08
2	−0.012
3	−1.26
4	−0.57
5	0.57
6	1.17
7	0.07
8	0.52
9	0.56
10–17	0.65–1.49

According to this definition of initial and final state energies, the enthalpy of reaction (3) will depend only on a difference of binding energies of nickel atoms in the cluster and in the molecular ion:

$$\Delta H = D(Ni_{n-1}–Ni) - D(Ni^+–Ni)$$

where $D(Ni_{n-1} - Ni) = \Delta(Ni_n) - \Delta(Ni_{n-1})$ is nickel atom escape energy from a cluster. Calculated values of ΔH for some n are given in Table 1. The D value is taken from [25]. It can be seen from Table 1 that reaction (3) will be endothermic for clusters with $n \geq 5$. Apparently this condition takes place in our experiments.

It is of interest to note that the similar results regarding ΔG^0 were obtained when different rates of heating (cooling) of sample were used. However, keeping in mind that the magnetic phase transition in the bulk occurs at 627.4 K, the Ni^+ intensity showed maximum at 620 ± 20 K during heating and at 550 ± 20 K during cooling, i.e. a temperature hysteresis was found to occur.

Assuming the dimers to form via the fragmentation mechanism we should take into account the probability of dissociation of Ni_2^+, so that Eq. (1) transforms to

$$I = AJCSP^+f$$

where f is the term describing the probability of the Ni_2^+ dissociation. In accordance with [27] we can determine the dependence of the latter term on the dissociation energy by

$$f(D) = [1 - \exp(-\alpha D)]$$

where α is a constant and D is the dissociation energy of Ni_2^+. Since $D = 2.08$ eV [25,26], it seems that f hardly depends on the temperature. Furthermore, it is obvious that the dissociation rate should increase with temperature, while the results (Fig. 2) show, on the contrary, an increase in the Ni_2^+ and Ni^+ intensity ratio as the sample temperature is increased. Therefore, the dissociation of the Ni_2^+ ions cannot be responsible for the temperature dependence of the secondary ion emission.

As mentioned previously, the influence of temperature on the Ni_2^+ and Ni^+ intensity ratio can not be attributed to temperature dependence of the parameters such as the sputter yield or the ionisation probability. But a change in impurity concentration on the surface with temperature may affect the work function and, hence, the secondary ion emission. However, according to Eqs. (1) and (2), the work function change should not result in any dependence of the Ni_2^+ and Ni^+ intensity ratio on temperature. Moreover, in the case of the fragmentation mechanism, one should expect a similar behaviour of the Ni_2^+ and Ni^+ ion emissions even near T_C, which, in fact, does not take place. Consequently, the dependence of the Ni_2^+ and Ni^+ intensity ratio on temperature cannot be explained within the framework of the fragmentation mechanism of dimer formation.

4. Conclusion

The influence of temperature on the Ni_2^+ and Ni^+ secondary ion emissions has been studied during Ar^+ and Xe^+ ion bombardment of polycrystalline nickel foil. The ferroparamagnetic phase transition at $T \cong 620$ K on nickel is found to have a considerable effect only on the emission of Ni^+. The Ni_2^+ dimers appear to form via the ion–molecule reaction occurring in the near surface region rather than by a direct ejection of lattice fragments. The change in Gibbs free energy of the reaction has been found to be equal to 0.061 ± 0.009 and 0.056 ± 0.007 eV for the cases of Ar^+ and Xe^+ primary ion beams, respectively. The results of this work support the recombination mechanism of the Ni_2^+ dimers formation.

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