State-resolved Study of keV Sputtered Neutral Atoms by Resonance Ionization Spectroscopy

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Abstract. We have performed simultaneous measurements of energy-, and angle-resolved distributions of Ni atoms desorbed from a single crystal Ni{100} surface bombarded by 5 keV Ar^+ ions. Ground state and six low-lying excited states from the a^3F_J (J = 4,3,2) and a^3D_J (J = 3,2,1) manifolds as well as a^1D_2 have been investigated along different azimuths. Both a^3F_J and a^1D_2 states have closed shell electronic structure, $3d^84s^2$, while the a^3D_J states are open shell electronic states, $3d^94s^1$. Angle-integrated energy distributions demonstrate a strong dependance on the electronic structure while the magnitude of the excitation energy does not significantly alter the results. This is the first conclusive evidence that electronic structure rather than excitation energy is the primary factor in determining kinetic energy distributions of sputtered neutral species. Population distribution among the seven electronic states are obtained through two sets of measurements performed on two experimental apparati: one measures the energy- and angle-integrated resonance ionization signal intensities of the sputtered Ni; the other measures the resonance ionization signal intensities of thermally evaporated Ni atoms with a known heating temperature. The experiment results show that the population distribution is very different from Boltzman-type distribution with a^3D_3 and a^3D_2 states more intensely populated. The work also illustrates the power of RIS to perform quantum state specific measurements on fast moving atoms.

INTRODUCTION

The interaction of energetic particles with surfaces is of fundamental interest.[1] Since an appreciable portion of the ejected particles are populated in electronic excited states, measurement of physical quantities as a function of each of the excited states should provide valuable information about excitation and deexcitation processes.[2-5] However, after more than two decades, many fundamental questions have not yet been answered.

In this contribution we present, for the first time, a systematic study of Ni atoms ejected from Ni{001} single crystals due to 5-keV Ar^+ ion bombardment.[6] We report on the velocity and population distributions of ejected neutral Ni atoms in 7 electronic states with different electronic configurations or term values and excitation energies. The reason for choosing Ni as a prototype target is due to its unique electronic structure. The lower electronic states of Ni are composed of triplet fine-structure states a^3F_J (J=4, 3, 2) and a^3D_J (J=3, 2, 1), and a singlet state

a^1D_2 with a^3F_4 as the ground state. As a transition metal, the three-fold a^3F_J states of Ni have electron configuration $3d^84s^2$, and are determined by the coupling of $3d$-electrons, not $4s$-electrons. In this case, the $2s$-electrons form a "closed-shell" and can effectively shield the d-electrons from interaction with the surface. On the other hand, the triplet a^3D_J and singlet a^1D_2 states of $3d^94s^1$ are formed when one s-electron is promoted from the 4s orbital to the $3d$ orbital. The electronic states are, in this case, formed by coupling between the $3d$-electrons and a $4s$-electron. As a consequence, the outer electrons are exposed, or in another words, form an "open-shell", and atoms in a^3D_J and a^1D_2 states readily interact with their environment. Obviously, if the excitation energy was the main factor which determines the relaxation rates of a state, then the state of higher excitation energy would show a larger degree of relaxation compared to a state of lower excitation energy.[2,6,7] The velocity distributions of atoms in these 7 electronic states are detected simultaneously by resonance ionization spectroscopy (RIS). The results show the velocity distributions of Ni atoms in these 7 states having different excitation energies can be sorted into two groups according to their electronic configuration. This demonstrates, for the first time, that the electronic shell structure is an important factor governing the inelastic relaxation or excitation processes.

Experimental

The measurement of angle-resolved velocity distributions is performed on an EARN apparatus which has been described in detail elsewhere.[8] The population distributions among different electronic states are obtained by combining data measured on the EARN apparatus and a specially designed high vacuum cell capable of producing gas phase Ni atoms through thermal evaporation.

Results and Discussion

The kinetic energy distributions of the measured Ni atoms in the open-shell states and closed-shell states are presented in Fig. 1. From these plots it is immediately evident that the velocity distributions of Ni atoms from different electronic states, with different excitation energies but with the same electronic shell structure, look very much alike. But velocity distributions of Ni atoms with different electron-shell structures are remarkably different.

There are two important, and quite different features between these two groups of states which merit special attention. First, the velocity distributions from a "closed-shell" are all peaked at the same value of 4.0 eV, which is about 1.0 eV smaller than those from the "open-shell" structure, all of which peak at 3.0 eV. This indicates that atoms having closed-shell electronic configurations more easily escape from the surface under Ar^+ bombardment than those having an opened-shell electron configuration. Presumably, these atom are effectively shielded by

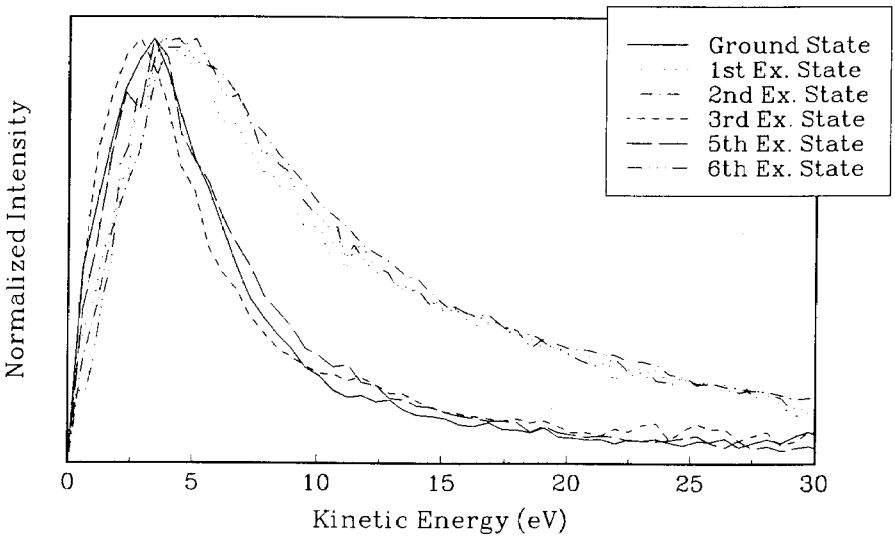

FIGURE 1. Velocity distributions of sputtered Ni atoms in the open-shell states a^3D_3, a^3D_2, and a^1D_2 and closed-shell state a^3F_4, a^3F_3, and a^3F_2 .

the filled *s*-orbital and they will not interact with the metal electrons at the Fermi level while departing from the surface. In another words, the effective surface binding energy is smaller for atoms having a closed outer shell orbital and is larger for atoms having an open outer shell orbital. Secondly, the atoms ejected which have open-shell state exhibit a broader kinetic energy distribution than those with a closed-shell configuration. The population distribution of different states can be readily obtained from the photoion signals measured on the EARN apparatus and the "heat-pipe" cell. For an initial state i, the MPRI signal via an intermediate state u can be expressed as

$$I_{iu}^{S} = N_i^{S}\,\Phi_{iu}(g_i,\ g_u,\ f_{iu},\ A_u,\ \sigma_u P)\eta^{S} \tag{1}$$

$$I_{iu}^{T} = N_i^{T}\,\Phi_{iu}(g_i,\ g_u,\ f_{iu},\ A_u,\ \sigma_u P)\eta^{T} \tag{2}$$

where, the superscript "S" represents quantities measured in the sputtering experiment and "T" represents quantities measured in the thermal evaporation experiment, I_{iu} is the signal intensity, N_i is the population, η is the detection efficiency, P is the laser fluence.

For initial states i and j ionized via a single upper state u, we can derive from Eqs. (1) and (2)

$$N_i^{S}/N_j^{S} = N_i^{T}/N_j^{T}\ \{I_{iu}^{S}/I_{ju}^{S}\}\ \{I_{ju}^{T}/I_{iu}^{T}\}. \tag{3}$$

TABLE 1. Relative population of sputtered Ni in different electronic states.

Ni Atom Initial State	*Energy (eV)*	*Popul. Dist. Sputtering*	*Boltzman Dist. at 956 °C*
a^3F_4	0	1	1
a^3D_3	.025	5.36	0.74
a^3D_2	.109	5.43	0.27
a^3F_3	.165	0.61	0.14
a^3D_1	.212	0.18	0.076
a^3F_2	.275	0.31	0.036
a^1D_2	.422	0.024	0.006

The relative populations of the sputtered Ni atoms in different states are listed in Table. 1. together with a Boltzman distribution at 956 °C. The most striking feature is the non-Boltzman-type distribution observed in the present experiment with a^3D_3 and a^3D_2 states more intensely populated than the ground state a^3F_4. Although discrepancies from the Boltzman-type distribution have been reported previously,[3,5,9] this is the first observation of population inversion for the sputtered particles. At present we are unsure of the mechanisms which underlie this phenomenon. However, we believe that there exists some selection rules for electron neutralization of the nuclei being sputtered from the solid into the vacuum.

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