PHYSICAL REVIEW B **73**, 075414 (2006)

Population inversion of metastable Ni atoms sputtered from Ni(100), Ni_3Al(100), and NiAl(110)

Ming Tan* and Bruce V. King
School of Mathematics and Physical Sciences, University of Newcastle, Callaghan NSW 2308, Australia

(Received 8 May 2005; revised manuscript received 16 November 2005; published 10 February 2006)

We have measured the ratio of the population of Ni neutral atoms sputtered into the a^3D_3 metastable state to that into the a^3F_4 ground state using two-color ionization schemes. The ratio is 2.27±0.31 for Ni, 2.34±0.17 for Ni_3Al, and 2.61±0.27 for NiAl. Within experimental error, we observed no effect of the valence band electron structure on the population ratio. We suggest that sputtered atoms should experience resonant neutralization and nonradiative relaxation. Before neutralization, departing Ni ions from the surface have an electron configuration of $3d^9$ or $3d^84s^1$. The 4*s* electron orbital of the departing ions captures a valence electron and formed nascent Ni atoms in the *D* ($3d^94s^1$) and *F* ($3d^84s^1$) states, respectively. The population inversion can be attributed to the character of ions and atoms of Ni. Because of the character of Ni ions, most of the ejected nascent Ni atoms are in the *D* state. The character of Ni atoms leads to a low relaxation rate of the *D* to *F* state. Many of the nascent Ni atoms in the *D* state can survive and so the population inversion was observed.

DOI: 10.1103/PhysRevB.73.075414 PACS number(s): 79.20.Rf, 34.50.Fa, 32.80.Fb

I. INTRODUCTION

The Winograd group found a very interesting result when sputtering the surface of Ni{100}.[1] The a^3D_3 excited metastable state is much more populated than the a^3F_4 ground state in the flux sputtered from the single crystal of Ni. The population ratio of a^3D_3 to a^3F_4 is more than 5. Later, Vandeweert *et al.* also observed the population inversion in polycrystalline Ni.[2] The population of the a^3D_3 metastable state is ~1.6 times that of the a^3F_4 ground state for polycrystalline Ni.

Winograd's group attributed the population inversion to the *d* band structure of the Ni metal. The effective occupation number of *d* like electrons in the Ni metal is around 9.[3] The electron configuration of Ni atoms in the metal is closer to a free Ni atom in the a^3D_3 state (electron configuration $3d^94s^1$) than to a free Ni atom in the a^3F_4 ground state ($3d^84s^2$). They argued that it is more likely that a sputtered atom is ejected in an electronic state (i.e., a^3D_3) closer to its state in the bulk.[4] Vandeweert *et al.* developed the idea and explained the population inversion in terms of the resonant electron transfer concept. They proposed that the wave function of Ni atoms in the a^3D_3 state has a better overlap with the bulk electronic wave function and this can enhance electron transfer into the a^3D_3 atomic state.[2,5]

Cortona *et al.*[6] have studied the influence of adsorbates, crystal structures, and target temperatures on the population and energy distributions of Ni atoms desorbed from sputtered Ni. They proposed that the density of states of a solid and the overlap of the wave functions of atoms with the wave function of the solid (bulk or surface) should play an important role in determining a population distribution and shaping an energy distribution.

Previous studies were focused on sputtering Ni metal. Little research has been undertaken on the alloys of Ni_3Al and NiAl. The *d* band structures of these two alloys differ from the Ni metal in the following two respects. First, the effective occupation electron number in the 3*d* orbital is 8.73 in the Ni_3Al alloy.[7] The 3*d* orbital of Ni atoms in NiAl is fully filled, containing ten electrons.[8] Second, the Fermi level of the Ni metal is in the *d* band while the Fermi level of the alloys is outside the *d* band. The *d* band lies approximately at 0.7 eV below the Fermi level of[7] Ni_3Al and at 1.5 eV for NiAl.[8] The main objective of this paper, therefore, is to measure the population partition of Ni atoms desorbed from sputtered Ni_3Al, NiAl and Ni and then to elucidate the *d* band structure effect on sputtering in metastable excited states. In the preliminary study,[9] we observed a very slight increase of the resonance ionization spectroscopy (RIS) signal ratio of Ni atoms in the a^3D_3 state to those in the a^3F_4 state in sputtering NiAl and attributed this increase to the band structure. In this paper, however, we have modified the previous view significantly after detailed experimental and theoretical analyses and proposed that the population inversion should be due to the characters of ions and atoms of Ni.

II. EXPERIMENTAL

A detailed description of the experimental apparatus and procedure for the laser post ionization surface analysis has been given in Ref. 10. Here we only briefly described the experimental procedure. The base pressure of the chamber was 1.0×10^{-9} mbar. The chamber pressure increased to 5×10^{-9} mbar when a pulsed Ar ion beam was incident onto the target surface. Argon ions were extracted from a Colutron model 101-Q ion source and were accelerated to 4 keV. The 4 keV argon ion beam was mass selected using a magnetic sector to eliminate impurities from the ion source and then steered onto the target by beam deflectors. The ion gun operated either in a continuous mode for *in situ* cleaning a target surface or in a pulsed mode for doing measurements. The variation of the ion pulse width ranged from 0.2 μs to 2.5 μs.

The primary ion pulse for the population measurements was a 2.0 μs long duration. Figure 1 gave the timing scheme for the population measurements of sputtered Ni atoms. The laser fired at $\tau_D=13.0$, 15.0, and 17 μs where τ_D was a delay time between the primary ion pulse and the laser pulse. Since

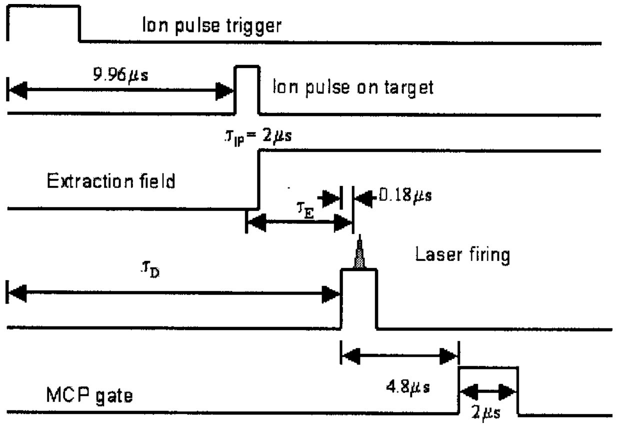

FIG. 1. Timing scheme of measuring the population of Ni atoms sputtered. The primary ions took 9.96 μs to arrive at the target. The duration of the primary ion pulse τ_{IP} is 2.0 μs. τ_D is a delay time between ion pulse trigger and laser trigger. The laser actually fires 0.18 μs after τ_D. The MCP gate is 2.0 μs wide. In a programmed population measurement, the laser fired at τ_D=13, 15, and 17 μs. When firing at τ_D=13 μs, laser ionizes sputtered atoms with τ_E in the range 1.2–3.2 μs where τ_E is a flight time of a sputtered atom from the surface to the laser beam. For this timing scheme, sputtered atoms with τ_E of 1.2–7.2 μs were detected, which include most of the sputtered atoms. Not drawn to scale

the primary argon ions took 9.96 μs to arrive at the target, the laser beam, when firing at τ_{D}=13.0, 15.0, and 17 μs, ionized sputtered atoms with τ_{E} in the range of 1.2–3.2, 3.2–5.2, and 5.2–7.2 μs, respectively where τ_{E} is a flight time of a sputtered atom from the surface to the laser beam. The photo ion yields at the above three delay times were integrated to give a relative population. The τ_{E} of sputtered atoms analyzed was in the range of 1.2–7.2 μs(0.83–30 eV). From the time of flight (TOF) spectra of sputtered Ni atoms from the alloys,[9] we can see that the τ_{E} range of most of the sputtered Ni atoms are in 1.2–7.2 μs.

Sputtered neutral Ni atoms were selectively ionized by two-photon resonance ionization. Photo ions were extracted to a time-of-flight mass spectrometer and counted by the dual microchannel plate detector. The two-color ionization schemes used for measuring the relative population of Ni atoms in the a^3D_3 and a^3F_4 atomic states are $a^3D_3 \rightarrow y^3F_4^0 \rightarrow$ autoionization (7.6817 eV) and $a^3F_4 \rightarrow y^3F_4^0 \rightarrow$autoionization (7.6817 eV), respectively.[2] The autoionization state lies at 0.04 eV above the ionization limit of Ni. The excitation wavelength for transition to the intermediate state $y^3F_4^0$ was 305.431 nm for the a^3D_3 atoms and 303.187 nm for the a^3F_4 atoms. The ionizing laser wavelength was 345.042 nm.

The second harmonic of a Nd:YAG laser (GCR-5A quanta-ray) pumped a lumonics HD-500 dye laser and a PDL-1 dye laser. The excitation photon was obtained from a frequency doubled output of the HD-500 dye laser and the ionization photon from a frequency double output of the PDL-1 dye laser. The excitation and ionization laser beams were focused and overlapped at a distance of 12 mm above the target surface. The laser energy was measured at the exit window of laser.

Before each measurement, the target surface was cleaned by bombarding with primary argon ions. Ionized sputtered neutral atom flux and therefore photoion intensity is sensitive to surface contamination. A less contaminated surface emits a greater fraction of neutral atoms when bombarded, and thus stronger photoion intensity was observed. Therefore the cleanliness of a target can be examined by measuring photoion intensity. Before a first measurement, an ion beam of 0.6 μA was continuously rastered into an area of 5.7 mm $\times$5.7 mm on a target surface for 40 min. For the measurements followed, the target was bombarded for 10 min before each measurement. Each measurement displayed almost the same photoion intensity. This means that, after initial sputtering of 40 min, the target became clean. This cleaning procedure was employed in all the measurements of population.

III. RESULTS

The relative population of Ni atoms sputtered into the a^3D_3 and a^3F_4 atomic states can be determined by the photoion yield using two-color ionization schemes. With the excitation transition saturated, the photoion yield n_i is given by[11]

$$n_i \approx n_0[1-\exp(-\sigma_{2i}\phi_2/2)], \qquad (1)$$

where n_0 is the population density of atoms in the state probed by the ionizing laser, σ_{2i} is the ionization cross section, and ϕ_2 the energy density of the ionizing laser. From Eq. (1) we can see that there are two requirements for the measurement of a relative population. First, the a^3D_3 atoms are excited to the same intermediate and autoionization states as the a^3F_4 atoms and the excitation transitions to the intermediate state are saturated. In this case, the cross section for ionizing the a^3D_3 and a^3F_4 atoms σ_{2i} is the same. Second, the ionization laser energy ϕ_2 is fixed. If these two requirements are met, then the measured photoion yields represent the relative population ($n_i \propto n_0$).

Figure 2 shows the saturation behavior of excitation transitions: a^3D_3-$y^3F_4^0$ and a^3F_4-$y^3F_4^0$. These measurements were conducted on Ni_3Al. The variation of photoion intensity with excitation laser energy was measured when ionization laser was operating at 0.13 mJ/pulse. The saturation of these two excitation transitions was achieved at laser pulse energies of about 1 mJ/pulse.

Figure 3 (upper, middle, bottom) shows photoion intensities of Ni atoms sputtered into the a^3F_4 and a^3D_3 states from Ni, Ni_3Al, and NiAl, respectively. With the ionization laser energy fixed at the laser pulse energy of 0.13 mJ/pulse, the excitation laser was operated at 1.5 mJ/pulse, which was strong enough to saturate the excitation transition. Thus the intensity of photoion represented a relative population. The contribution of one-color ionization to a total photoion yield was 2% for the a^3F_4 atoms and 3% for the a^3D_3 atoms in our ionization schemes, which were neglected. Four independent measurements were conducted for a relative population of atoms sputtered into the ground and excited states. We took Fig. 3 (upper, Ni) and Fig. 3 (middle, Ni_3Al) as examples to illustrate the measurement details. Upon cleaning the surface of Ni_3Al, we alternatively measured the population of the a^3F_4 ground state and the a^3D_3 metastable state four times. Here we like to point out that, before each measurement, we

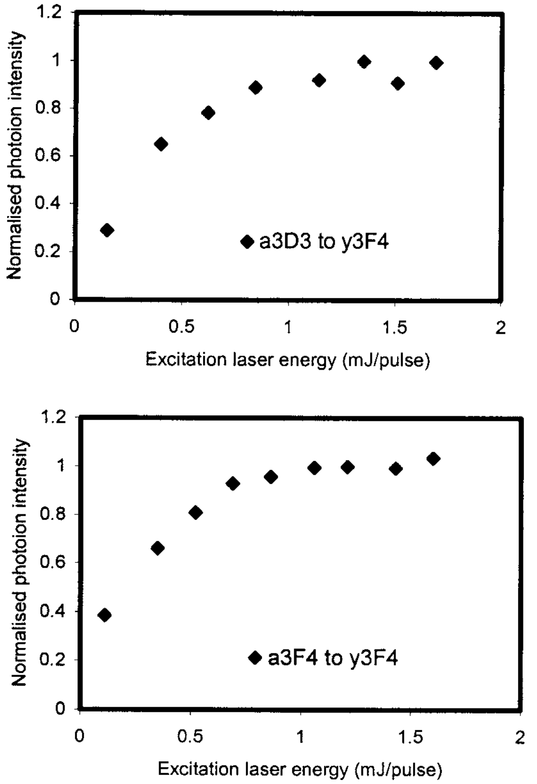

FIG. 2. The saturation behavior of excitation transitions: (upper) a^3D_3-$y^3F_4^0$ and (bottom) a^3F_4-$y^3F_4^0$. These measurements were conducted on Ni_3Al.

cleaned the surface to reduce the effect of contamination on the population ratio. The sample holder held two samples. After finishing the measurements on Ni_3Al, we vertically translated the sample holder so that the populations from pure Ni can be measured. Under such experimental conditions, the measurement error due to the fluctuation of laser beam and ion pulse should be reduced. Our results are well reproducible. After completing the measurements on Ni_3Al and pure Ni, we took out Ni_3Al and loaded NiAl into the chamber and baked out the chamber. We performed measurements not only on NiAl but also on pure Ni. The experimental procedure of measuring the populations of NiAl and pure Ni was the same as that of Ni_3Al and pure Ni. We first measured the populations from NiAl; and then vertically translating the sample holder, measured the populations from pure Ni again. The population ratio of pure Ni we obtained this time was the same as that obtained before.

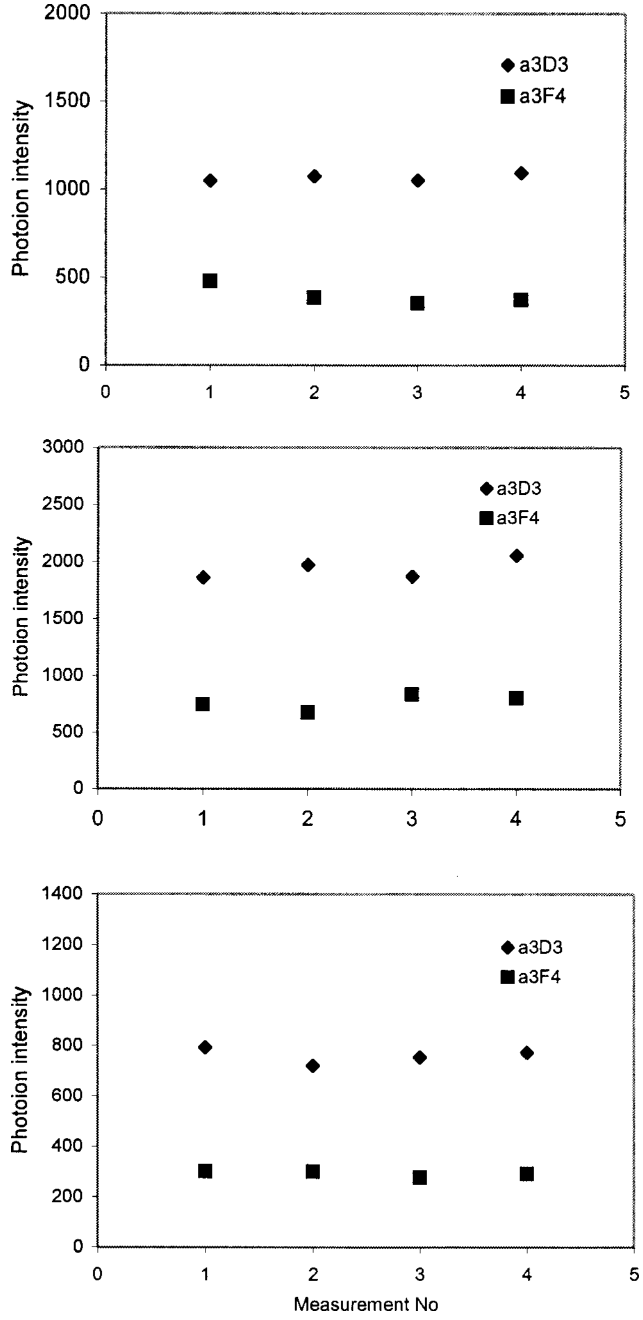

FIG. 3. Photoion intensities of Ni atoms sputtered into the a^3F_4 ground state and a^3D_3 metastable states: (upper) Pure Ni, (middle) Ni_3Al, and (bottom) NiAl. These measurements were performed with the ionization laser energy fixed at 0.13 mJ/pulse and the excitation laser operated at 1.5 mJ/pulse.

For all the targets, the a^3D_3 metastable state was much more populated than the a^3F_4 ground state. The population ratio of a^3D_3 to a^3F_4 was determined to be 2.27 ± 0.31 for Ni from Fig. 3 (upper), 2.34 ± 0.17 for Ni_3Al from Fig. 3 (middle) and 2.61 ± 0.27 for NiAl from Fig. 3 (bottom). It appeared that the population ratio of NiAl was slightly higher than that of pure Ni and Ni_3Al. However, we believed that these three samples should have the same population ratio after taking into account the following two factors. First, Cortona *et al.*[6] found that the oxidation of Ni surface resulted in an increased population ratio of a^3D_3 to a^3F_4. Second, our measurements were performed in pulsed mode with an operating pressure of $\sim 5 \times 10^{-9}$ mbar. In this case, very small surface contamination can occur during a 2 min population measurement. We found from the decay of a resonance ionization signal with time that NiAl was more easily contaminated than Ni and Ni_3Al. Therefore, the observation that NiAl had a slightly higher population ratio was possible due to the slightly more contamination occurring during measurements. For the Ni metal, the population ratio we obtained (2.27) is larger than the ratio Vandeweert *et al.*

obtained[2] (1.6) but smaller than the ratio He *et al.* reported (5.7).[1]

Our measurement system can display not only the population sputtered into an atomic state but also in the mean time the angular distribution of atoms sputtered into this atomic state. The observed photoion images show that the angular distributions sputtered from these three samples are different from each other. However, there is no difference in angular distribution between the a^3D_3 and a^3F_4 states for each surface. Therefore, a population ratio is not dependent on an angular distribution.

We have also measured the ratio of the resonance ionization spectroscopy (RIS) signal from the a^3D_3 state to that from the a^3F_4 state for Ni, Ni_3Al, and NiAl using a resonant one-color scheme, exciting through the same intermediate level. A RIS ratio does not represent a population ratio directly, since the ionization transition goes to different final states. However, by alternatively measuring pairs of samples under the same laser and ion beam conditions, the change of the population ratio can be reflected in the RIS ratio. This can be understood from the following argument. The RIS signal intensity is given by $I_{RIS}=nVP$ where n is the population density that indicates the number per unit volume at the laser beam region of atoms emitted in a specific quantum state. V is the sampling volume and P is the ionization probability of one atom in the laser field. Since the experimental conditions for the Ni_3Al and NiAl alloys such as the primary ion pulse and the laser pulse energies were the same as those for the Ni metal, the V ratio for the alloys $(V_{a^3D_3}/V_{a^3F_4})_{alloys}$ was identical to that of the metal, $(V_{a^3D_3}/V_{a^3F_4})_{metal}$. The V ratio was equal to 1 since the laser energy for ionizing the a^3F_4 atoms was the same as that for ionizing the a^3D_3 atoms. We do not know the ionization probability P. However, the P ratio of the alloys $(P_{a^3D_3}/P_{a^3F_4})_{alloys}$ is also the same as that of the metal, $(P_{a^3D_3}/P_{a^3F_4})_{metal}$ because the laser energy and ionization schemes for ionizing the a^3F_4 and a^3D_3 atoms remain unchanged for all three samples. Therefore, the change of RIS signal intensity ratio $\Delta(I_{a^3D_3}/I_{a^3F_4})$ can unambiguously reveal the change of the population ratio $\Delta(n_{a^3D_3}/n_{a^3F_4})$.

The timing scheme for measuring the RIS ratio was the same as that for measuring the population ratio. The one-color ionization schemes used in our measurements were $a^3D_3 \rightarrow y^3F_3^0 \rightarrow$ ionization and $a^3F_4 \rightarrow y^3F_3^0 \rightarrow$ ionization. The laser energy used was about 1 mJ/pulse. The RIS ratio of a^3D_3 to a^3F_4 was 1.05 ± 0.12 for pure Ni, 1.07 ± 0.09 for Ni_3Al and 1.19 ± 0.1 for NiAl, respectively.

Within experimental error, we observed no difference between the alloys and the metal in the relative sputter yield of Ni atoms in the a^3D_3 metastable excited state compared to the a^3F_4 ground state, in both one color and two color ionization experiments.

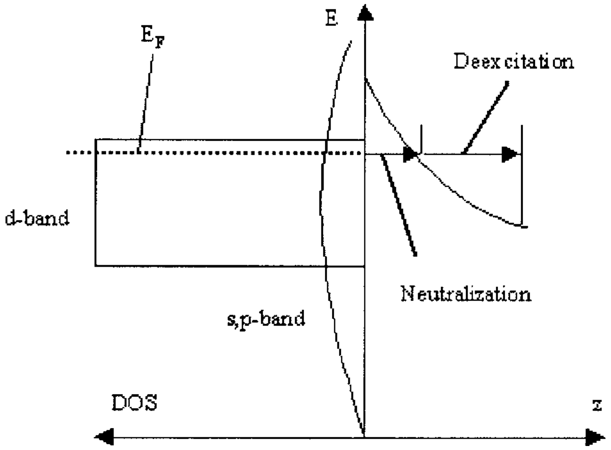

FIG. 4. The right side of this figure is a schematic energy diagram for a particle sputtered from a metal surface. The z axis is the distance between the departing particle and surface and the E axis is the energy of the atomic level. The energy of the atomic level is a function of the distance from the surface due to the image charge effect. In the neutralization region, a departing ion captures a valence electron by a tunneling process. In the deexcitation region, excited nascent Ni neutral atoms can experience nonradiative deexcitation. The left side of this figure schematically gives the calculated density of states (DOS) of s-p and d bands of Ni metal. The Fermi level E_F is in the d band. The delocalized electrons in the s-p band play an important role in the resonant neutralization.

IV. DISCUSSIONS

We can explain the above results in terms of the resonant electron transfer and nonradiative deexcitation concept. We suggest that lattice Ni ions leaving from lattice sites could undergo two processes, as shown in the right side of Fig. 4. First, a single-charged departing Ni positive ion can pick up an electron from the valence band by a tunneling process. Second, the nascent Ni neutral atoms, when in excited states, can experience nonradiative deexcitation. These two processes take place in the interaction region as shown in the right side of Fig. 4. Outside the interaction region, the departing particles are free particles. Here we will discuss the resonant electron transfer and nonradiative deexcitation separately.

A. Resonant electron transfer

Electron tunneling has been proposed to be a possible electronic process which occurs during sputtering by Yu,[12] Veje,[13] and Lievens *et al.*[5,14] When an atom is sputtered from the metal, resonant electron transfer can take place between its atomic level and the delocalized state of the valence band. As a first approximation, the tunneling probability depends on the overlap of the atomic state wave function with valence electron wave function. The larger the overlap between the wave functions of the sputtered atom and the valence electron is, the larger the tunneling probability is.

Electron tunneling is a single electron process and thus before neutralization the departing Ni positive ions must be singly charged positive ions. Since the free Ni ions with the $3d^9$ and $3d^84s^1$ electron configuration have lower energies,[15] we assume that the electron configurations of the departing single charged Ni positive ions can be like $3d^9$ and $3d^84s^1$.

In the following, we will consider two questions. First, which empty electron orbital of a departing ion has captured an electron from the valence band? Second, what was the concentration of Ni ions with the $3d^9$ and $3d^8 4s^1$ electron configurations before neutralization?

It can easily be seen from the geometric shape of $3d$ and $4s$ electron wave function[16] that the $4s$ electron wave function has a much greater overlap with the valence electrons of the metal surface than the $3d$ electron wave function. We therefore believe that valence electrons can dominantly transfer to $4s$ electron orbital when Ni ions with a $3d^9$ and $3d^8 4s^1$ electron configuration depart from the surface and the $3d^9$ and $3d^8 4s^1$ Ni ions are the precursors of the nascent Ni atoms in D and F states, respectively.

Understanding the relative concentration of $3d^9$ and $3d^8 4s^1$ Ni ions before neutralization can help elucidate the population distribution of Ni atoms. In transition-metal atoms the $4s$ orbital is usually more stable than the $3d$ orbital, while in positive ions the reverse is true.[17] For positive Ni ions, for example, the ground state electron configuration is $3d^9$ while the excited state electron configuration is $3d^8 4s^1$ with the excitation energy of more than 1.0 eV.[15] Therefore, the concentration of $3d^9$ ions prior to neutralization should be much larger than that of $3d^8 4s^1$ ions during sputtering Ni metal and alloy and the nascent Ni atoms in the D state dominate in number over those in the F state.

The metal and alloy can be visualized as a system with positive ions immersed in a valence electron sea. When an ion in a metal or alloy leaves a lattice position due to a collision, its original electron configuration will be changed. For example, the Ni atoms in the lattice sites of the NiAl alloy have an electron configuration of $3d^{10}$. At the moment the $3d^{10}$ Ni atom is deviated slightly from a lattice site, its $3d$ electron configuration would immediately experience an electron transition for two reasons. First, when Ni atoms are not in the lattice site, the electron configuration with the lowest energy is not $3d^{10}$ since the "environment" of these atoms are different from that in the lattice sites. Second, the electron transition in metal or alloy is very rapid. The relaxation time of the valence electrons is very short[13] ($10^{-19}-10^{-15}$ s) and the charge transfer occurs within 10^{-15} s or less.[18,19] The velocity of the recoiling ion that will leave a lattice site as a sputtered particle is on the order of 10^6 cm/s. In the relaxation time period of 10^{-15} s, the recoiling ion moves a distance of 0.01 nm, about 3% of the lattice ion spacing ($\sim$0.3 nm). This means that when lattice ions deviate slightly from lattice sites, they will have an electron configuration that is different from the original electron configuration. The electron configuration of the recoiling ion is constantly changing to minimize its energy. Since the $3d^9$ Ni ion has the lowest energy and the $3d^8 4s^1$ ion has an excitation energy of more than 1.0 eV,[15] the electron configuration of the Ni ion that is removed from the lattice site of the NiAl alloy is much more likely to evolve to the $3d^9$ electron configuration than to the $3d^8 4s^1$ electron configuration. This leads to one conclusion. The valence electron structure of the metal and alloys should have little effect on the ratio of the concentration of the $3d^9$ ions to that of the $3d^8 4s^1$ ions and thus on the ratio of the concentration of the nascent $3d^9 4s^1$ atoms to that of the nascent $3d^8 4s^2$ atoms.

B. Nonradiative deexcitation and population inversion

The nascent neutral atoms formed at the moment of neutralization have atomic features but they are not free atoms when flying in the interaction region. The $4s$ and $3d$ electrons of the escaping nascent Ni atoms still have an interaction with the valence electrons. It is the interaction that induces the nonradiative deexcitation. For Ni atom, the $3d^8 4s^2$ configuration is more stable than the $3d^9 4s^1$ configuration.[15,17] Therefore, some of the $3d^9 4s^1$ nascent Ni atoms can relax to the $3d^8 4s^2$ atoms.

Before making further discussion of our results, we should briefly discuss the nonradiative deexcitation theory. The early theory[12] said that the nonradiative events depend mainly on the excitation energy. The more recent theory of Craig *et al.*[20] suggest that the nonradiative relaxation is determined largely by the electron configuration of an atom in excited state. However, our results for sputtered Al atoms indicate that the deexcitation rate can be related to the excitation energy.[10] Energy levels of the first metastable excited multiplet $D_J(3d^9 4s^1)$ are intertwined with the energy levels of the ground multiplet $F_J(3d^8 4s^2)$ of Ni. The excitation energy of the metastable excited multiplet D_J is small. For example, the Ni atoms in the a^3D_3 state have a small excitation energy value of 0.03 eV. Because of both the small excitation energy and the electron configuration of $3d^9 4s^1$ with partial shielding, we expected that the relaxation rate of the D atomic state to F atomic state is slow.

In Sec. IV A we have demonstrated that the character of Ni ions results in dominant nascent Ni atoms in the D state in the sputtered flux. The character of Ni atom causes a slow relaxation rate of the D atomic state to the F atomic state. Therefore a larger fraction of the Ni atoms in D states can survive and the population inversion was observed in the flux sputtered from the Ni metal and alloys.

V. CONCLUSIONS

In the sputtered flux, the ratio of the population of Ni neutral atoms sputtered into the a^3D_3 metastable state to that into the a^3F_4 ground state was 2.27 ± 0.31 for Ni, 2.34 ± 0.17 for Ni_3Al, and 2.61 ± 0.27 for NiAl. Within experimental error, we observed no effect of the valence band electron structure on the population ratio. The ratio of the RIS of Ni atoms in the a^3D_3 metastable state to that in the a^3F_4 ground state from the one-color ionization schemes corroborated this observation.

Our results of the population of sputtered Ni atoms can be explained in terms of the resonant electron transfer and nonradiative relaxation. The population inversion observed on Ni, Ni_3Al, and NiAl can be attributed to the characters of ion and atom of Ni, independent of the valence electronic structure.

*Permanent address: College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China. Electronic address: tanming@phy.ccnu.edu.cn

[1] C. He, Z. Postawa, S. W. Rosencrance, R. Chatterjee, B. J. Garrison, and N. Winograd, Phys. Rev. Lett. **75**, 3950 (1995).

[2] E. Vandeweert, V. Philipsen, W. Bouwen, P. Thoen, H. Weidele, R. E. Silverans, and P. Lievens, Phys. Rev. Lett. **78**, 138 (1997).

[3] D. A. Papaconstantopoulos, *Handbook of the Band Structure of Element Solids* (Plenum, New York, 1986).

[4] C. He, Z. Postawa, M. El-Maazawi, S. Rosencrance, B. J. Garrison, and N. Winograd, J. Chem. Phys. **101**, 6226 (1994).

[5] P. Lievens, V. Philipsen, E. Vandeweert, and R. E. Silverans, Nucl. Instrum. Methods Phys. Res. B **135**, 471 (1998).

[6] A. Cortona, W. Husinsky, and G. Betz, Phys. Rev. B **59**, 15495 (1999).

[7] T. Nautiya and S. Auluck, Phys. Rev. B **45**, 13930 (1992).

[8] S. C. Lui, J. W. Davenport, E. W. Plummer, D. M. Zehner, and G. W. Fernando, Phys. Rev. B **42**, 1582 (1990).

[9] M. Tan and B. V. King, Appl. Surf. Sci. **203-204**, 248 (2003).

[10] M. Tan and B. V. King (unpublished).

[11] V. S. Letokhov, *Laser Photoionization Spectroscopy* (Academic, Orlando, 1987).

[12] M. L. Yu, *Sputtering by Particles Bombardment III* (Springer-Verlag, Berlin, 1991).

[13] E. Veje, Phys. Rev. B **28**, 5029 (1983).

[14] R. E. Silverans and P. Lievens, in *Resonance Ionization Spectroscopy*, edited by J. C. Vikerman, I. Lyon, N. P. Lockyer, and J. E. Parks, 9th International Symposium on Resonance Ionization Spectroscopy, Manchester, UK, 1998, p. 197.

[15] Yu. Ralchenko, A. E. Kramida, and J. Reader, NIST Atomic Spectra Database, Version 3.0.3, 2005 (unpublished).

[16] C. H. Hurd, *Electrons in Metals* (Wiley, New York, 1975).

[17] W. G. Richards and P. R. Scott, *Energy Level in Atoms and Molecules* (Oxford Science Publication, Oxford, 1994).

[18] O. Gunnarsson and K. Schonhammer, Solid State Commun. **26**, 147 (1978).

[19] P. Feulner and D. Menzel, in *Laser Spectroscopy and Photochemistry on Metal Surfaces*, edited by H. L. Dai and W. Ho (World Scientific, Singapore, 1995), p. 627.

[20] B. I. Craig, J. P. Baxter, J. Singh, G. A. Schick, P. H. Kobrin, B. J. Garrison, and N. Winograd, Phys. Rev. Lett. **57**, 1351 (1986).