Space- and time-resolved optical spectroscopy of plumes generated by laser ablation of NiO in a vacuum

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Laser ablation of NiO at 266 nm has been studied by measuring absorption spectra and emission spectra which are resolved both temporally and spatially. The spectra were measured at several points 1 mm apart from the laser spot and with several detection angles. Ablated species in different electronic states such as the ground state, lower lying states, and excited states are distinguished from absorption and emission spectroscopy. Time-of-flight spectra of these species and their angular dependence are obtained. It is revealed that excited Ni neutrals are generated mainly by the recombination of Ni⁺ ions with electrons, and Ni⁺ ions ejected nearly normal to the surface are exclusively excited due to multiple collisional effect. The isotropic angular dependence of most probable velocities of Ni⁺ ions and Ni neutrals are explained by ambipolar diffusion of the plume. The mechanism of species ejection is also discussed. © 1998 American Institute of Physics. [S0021-8979(98)03306-4]

I. INTRODUCTION

Transition metal oxides with NaCl-type structure have been extensively studied for a variety of applications as electronic materials due to excellent optical, electrical, and magnetic properties. Each oxide has some phases depending on temperature and oxygen partial pressure. Coexistence of some phases may diminish reproducibility of the physical properties, and is not suitable for actual application. Exceptionally, nickel oxide has a monoxide phase over a wide range of conditions.¹ There are many reports on the preparation of NiO thin films in connection with the application as electronic materials. Methods of film formation are evaporation, rf sputtering, molecular beam epitaxy, metalorganic chemical vapor deposition, and pulsed laser deposition (PLD).² Among them, PLD has several advantages over conventional methods: small compositional changes, versatility, high speed film formation, and high controllability with pulse number, pulse energy, and ambient pressure.³ Meanwhile, surface resistivity of sintered NiO is sensitive selectively to the irradiation of atomic beams, but not to the irradiation of molecular beams.⁴ Moreover, NiO thin films formed by PLD are found to be more sensitive to atomic beams than single crystal.⁵ Therefore, film formation of NiO of good quality is desired for the application as an atomic beam sensor.

It is generally accepted that highly excited species with high kinetic energy produced by laser ablation play an important role in forming thin films of good quality. Furthermore, it was reported that a bias voltage applied to the sub-

strate affects the film quality, which means that ionic species also play an important role in film formation.⁶ The quality of films thus depends on the distribution of the internal energy and kinetic energy of ions and neutrals in the laser-produced plasma which is called a plume. It is then helpful for improving the film quality to elucidate the structure of a plume and its evolution. Considerable studies on the basic ablation mechanism have so far been made especially because of a great interest in high- T_c superconductive oxides. Optical spectroscopy⁷⁻¹⁷ and quadrupole mass spectroscopy,^{6,18,19} which provides time-of-flight (TOF) spectra of the species, has been frequently employed for these studies. However, involved phenomena of PLD have been poorly understood and film formation is still performed in a trial and error manner. Recently, fundamental processes of the laser ablation were discussed from angle-involved time-of-flight mass spectra and angle-resolved yield distributions of the ejected species.^{18,19} In this case, species were observed far away from the target. On the other hand, optical spectroscopy provides information about the species near the target, and the early stage of the expansion of laser-produced plasma.

This study is devoted to elucidate dynamic processes of the laser ablation by using optical spectroscopy. Optical emission spectroscopy is used to roughly monitor the evolution of laser-produced plume.⁷⁻¹⁰ We have already studied expansion of the plume from NiO by this method.²⁰ However, in the optical emission spectroscopy, one detects only luminescent species whose electrons occupy higher electronic states, although dominant species in the plume are known to be in the ground state.³ On the other hand, intensity of absorption which corresponds to electronic transition from the ground state or lower lying states is more directly proportional to the density of species.¹¹⁻¹⁴ Moreover, multichan-

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FIG. 1. Schematic diagram for spatially and temporally resolved absorption spectroscopy and emission spectroscopy.

nel measurements employed in this study allow us to detect different species in different electronic states at the same time. Furthermore, these absorption and emission spectra are spatially and temporally resolved in this study, which yields angular dependencies of the velocities and number densities of luminescent and nonluminescent species. Meanwhile, optical emission intensity depends not only the density of species but also excitation processes, so that measurements of both absorption and emission spectra reveal the excitation processes of the species. The mechanisms for ejection of species from the target surface, expansion of the plume, and excitation of the species are discussed from the obtained results.

II. EXPERIMENT

Powdered NiO (99.9%) was supplied from Rare Metallic Co. They were ground into fine powders and compressed to pellets, which were subsequently sintered at 1200 °C for 3 h. On the basis of the phase diagrams,¹ the obtained pellets of nickel oxide are expected to be NiO. The typical dimension of the pellets was 9 mm in diameter and 2.5 mm in thickness.

Schematic diagram of the measurement system is shown in Fig. 1. The fourth harmonic of Nd:YAG pulsed laser ($\lambda = 266$ nm, 6.5 ns, 10 Hz) was used for the film formation⁵ because the photon energy is larger than the absorption edge of NiO (4.5 eV)²¹ and photochemical processes are expected to be dominant. The laser beam was separated by a Pellin Broca prism and introduced into a high vacuum chamber, whose base pressure was 1×10^{-4} Pa, and focused into a spot of 0.1 mm ϕ on the rotating pellet (0.5–1 turns/s). Optimum laser fluence for thin film formation was found to be about 5 J/cm²,⁵ so that the laser fluence for the optical measurements was 5.1 J/cm² in most cases. Laser fluences of 2.5 and 50 J/cm² were also used to observe the phenomenon near the ablation threshold and to detect O⁺ ions, respectively. Optical system collecting emission spectra and absorption spectra consist of mirrors so as to avoid the chromatic aberration which, as pointed out in Ref. 20, so far should have reduced spatial resolution in a lot of spectroscopic studies reported.

In the emission measurement, the image of the plume was projected onto the entrance slit of a monochromator with a magnification of 2. In the absorption measurement, the

FIG. 2. Projection view around the target surface. Points A, B, C, and D are located on a circle with a center at the laser spot and with a radius of 1 mm. The angles θ between the surface normal (OA) and OB, OC, and OD were 15°, 30°, and 45°, respectively. The optical path penetrates the 25 $\mu\text{m} \times 25 \mu\text{m}$ cross section at these points.

plume was illuminated by a Xe flash lamp (EG&G Electro-Optics Inc., FX1152) whose duration was about 1 μs . The transmitted image was projected onto the entrance slit by the same optical system as the emission measurement. The emission light and transmitted light was dispersed by a monochromator (ARC Spectra Pro 275) with a 300 nm blazed grating of 1200 grooves/mm. The slit width of the monochromator was 50 μm , which corresponds to a resolution of 0.15 nm. Output spectra was then temporally dispersed with a streak camera (Hamamatsu C2830). Detectable wavelength range was from 200 to 850 nm. The temporally dispersed spectra was monitored with a cooled CCD camera (Hamamatsu C3140). Typically, images accumulated over 1000 laser shots were recorded. The slit width of the entrance slit of the streak camera was 50 μm . Therefore, the light projected in a 50 $\mu\text{m} \times 50 \mu\text{m}$ square was spectrally and temporally dispersed. The images on the entrance slit of the monochromator was magnified by 2, so that the spatial resolution of the detection system was 25 $\mu\text{m} \times 25 \mu\text{m}$ at the plume.

The projection view around the target surface was depicted in Fig. 2. Needle-like white plasma of about 0.5 mm was formed normal to the target surface at the laser fluence of 5.1 J/cm². Spectra of the plume was measured through long rectangular prisms which are perpendicular to the projection view and located at four points, A, B, C, and D. Squares at these points represent 25 $\mu\text{m} \times 25 \mu\text{m}$ cross section of these rectangular prisms. Four points are located on a circle with a center at the laser spot and with a radius of 1 mm, that is, well outside of the needle-like plasma. The point A is on the surface normal. Angles θ between the surface normal and OB, OC, and OD are 15°, 30°, and 45°, respectively.

III. RESULTS

Temporally resolved spectrograms measured at point A and at the laser fluence of 5.1 J/cm² are shown in Fig. 3. The horizontal axes correspond to wavelengths ranging from 228 to 236 nm, whereas the vertical axes correspond to time measured from the peak of the laser pulse which is indicated by

FIG. 3. Temporally resolved spectrograms measured at point A and at the laser fluence of 5.1 J/cm^2 . (a) and (b) are represented by a grey scale of the spectrograms of transmittance intensity and emission intensity, respectively. White horizontal lines represents the time of the laser pulse. Spectral lines involved in this wavelength range are due to Ni^+ ions and Ni neutrals.

white lines. Figure 3(a) was obtained as follows. At first, the output of each pixel of the CCD image due to transmitted light was divided by the output of the corresponding pixel of the image due to the Xe flash lamp only. Thus, the obtained image was then zero suppressed so as to make dark lines clear. The dark lines in Fig. 3(a) mean that incident light is absorbed for some duration at specified wavelengths due to electronic transitions from the ground state or lower lying states to excited states. The dark lines located at 229.71 and 230.30 nm are only seen for about 100 ns, whereas other dark lines seem to survive for more than $1 \mu\text{s}$. The former lines are attributed to electronic transitions from a^4F' states to a^4D' states of Ni^+ ion,²² whereas the latter lines are attributed to those from a^3F states to w^3F^o , w^3D^o , y^3G^o , and x^3D^o states of Ni neutral.²³ In this way, temporally resolved absorption spectra due to Ni^+ ions and Ni neutrals are observed at the same time by the multichannel spectroscopy. The wavelengths of these lines, corresponding electronic transitions, energies of lower states, and lifetimes of upper states²⁴ are listed in Table I. The a^3F states of Ni neutral are the electronic ground state, however, the a^4F' states of Ni^+ ion are lower lying states located about 1.0 eV higher than the ground a^2D state.²⁵ Transitions from the a^2D state appear only in vacuum ultraviolet range. Dark lines due to Ni neutrals in Fig. 3(a) are not clear in the range above 800 ns after the laser pulse, because the duration of the Xe flash lamp is about $1 \mu\text{s}$. When the Xe lamp is flashed $1 \mu\text{s}$ after the laser pulse, the dark lines are clearly observed even in the range above $2 \mu\text{s}$. Absorption due to transitions from the ground a^3F states of Ni neutrals were also measured in the

TABLE I. Absorption and emission lines which are analyzed.

Species	Wavelength (nm)	Transition	E_{lower} (eV)	Lifetime (ns)
Ni	231.10	$a^3F_4 - w^3F_4^o$	0.00	
Ni	231.23	$a^3F_3 - w^3F_3^o$	0.17	1.8
Ni	231.40	$a^3F_2 - w^3F_2^o$	0.27	
Ni	231.72	$a^3F_3 - w^3D_2^o$	0.17	2.6
Ni	232.00	$a^3F_4 - y^3G_5^o$	0.00	1.4
Ni	232.14	$a^3F_2 - y^3G_3^o$	0.27	
Ni	232.58	$a^3F_3 - y^3G_4^o$	0.17	2.9
Ni	234.56	$a^3F_4 - x^3D_3^o$	0.00	4.5
Ni^+	229.71	$a^4F'_3 - a^4D'_2$	1.25	2.2
Ni^+	230.30	$a^4F'_4 - a^4D'_3$	1.16	2.1
Ni^+	231.60	$a^4F'_5 - a^4D'_4$	1.04	2.0
Ni^+	233.46	$a^2F'_4 - a^2G'_4$	1.68	7.7
Ni^+	234.12	$a^2P'_2 - c^2D'_3$	3.60	
O	777.19	$3s^5S_2^o - 3p^5P_3$	9.14	29
O	777.42	$3s^5S_2^o - 3p^5P_2$	9.14	29
O	777.54	$3s^5S_2^o - 3p^5P_1$	9.14	29

wavelength range from 335 to 365 nm. Temporal distribution of these absorption lines is the same as those of Ni neutrals in Fig. 3(a).

Figure 3(b) shows a temporally resolved optical emission spectrogram. The scale of the vertical axis corresponding to time after the laser pulse is one-fifth of that of Fig. 3(a), although the horizontal axis is the same. There are more lines in Fig. 3(b) than in Fig. 3(a), because electronic transitions between excited states as well as transitions to the ground state or lower lying states are observed in the emission spectra. For example, emission lines located at 233.46 and 234.12 nm are due to transitions between excited states of the Ni^+ ion. These emission lines are also listed in Table I. As is easily seen, optical emission from the Ni^+ ion is observed for shorter duration than that from Ni neutral. It is common to Fig. 3(a) that Ni^+ ion lines are shorter than those of Ni neutral lines. Taking into account that the scale of the vertical axis of Fig. 3(b) is one-fifth of Fig. 3(a), one notes that emission lines are observed for much shorter duration than corresponding absorption lines.

Optical emission from O neutral is observed dominantly around 777.5 nm, which is attributed to electronic transitions between excited $3s^5S_2^o$ and $3p^5P$ states.²⁶ Absorption due to transitions from the ground state of O neutral appears only in the vacuum ultraviolet range. Any trace of O^+ ions was not observed at the laser fluence below 5.1 J/cm^2 , although emission lines of O^+ ion are dominant at the fluence of 50 J/cm^2 . The reason why emission lines of Ni^+ ions are observed and those of O^+ ions are not observed at the fluence of 5.1 J/cm^2 is probably that the ionization potential of the O neutral (13.617 eV)²⁵ is about twice higher than that of Ni neutral (7.606 eV).²³ Meanwhile, absorption and emission lines due to NiO molecules are expected to be observed in the wavelength range from 550 to 630 nm corresponding to transitions between the ground $X^3\Sigma''$ state and excited states.^{27,28} However, they were not observed at any fluences from 2.5 to 50 J/cm^2 .

Figure 3(a) was obtained after zero suppression to make dark lines clear. The image without this zero suppression

FIG. 4. TOF spectra of (a) Ni^+ ions at 229.71 nm, (b) Ni neutrals at 232.00 nm and (c) O neutrals at 777.5 nm. They are measured at point A and at the laser fluence of 5.1 J/cm^2 . Solid and dashed lines correspond to absorbance and emission intensity, respectively.

should correspond to a temporally resolved transmittance spectrum. However, even if there are no absorption lines, a uniform image is not obtained because of jitters of the Xe flash lamp. Accordingly, temporally resolved absorbance of an absorption line is defined as $\alpha(t) = \log[T_0(t)/T(t)]$, where $T(t)$ is a temporal variation of the transmitted light intensity of the absorption line in the image without the zero suppression and $T_0(t)$ is that of the background line close to the absorption line. On the other hand, temporally resolved emission intensity $I(t)$ of an emission line is simply defined as the temporal variation of the intensity of the emission line. $\alpha(t)$ corresponds to a time-of-flight (TOF) spectrum of a species in the ground state or lower lying states, whereas $I(t)$ corresponds to a TOF spectrum of an excited species. Figure 4(a) shows $\alpha(t)$ and $I(t)$ of Ni^+ ions at 229.71 nm ($a^4F'_3 - a^4D'_2$ transition), and Fig. 4(b) shows those of Ni neutrals at 232.00 nm ($a^3F_4 - y^3G_5^o$ transition). Figure 4(c) shows only $I(t)$ of O neutrals at 777.5 nm ($3s^5S^o_2 - 3p^5P$ transition). The TOF spectra in Fig. 4 are observed at point A, that is, on the surface normal. The $\alpha(t)$ spectrum of Ni

neutrals has been obtained by smoothing over 30 ns. Several points are noted in Fig. 4. Hereafter, * and ' superscripts are used to designate excited states and lower lying states, respectively. The names of species without these superscripts represent the species in the ground state. First, $\text{Ni}^{+'}$ ions move faster than Ni^* neutrals, and $\text{Ni}^{+'}$ ions move faster than Ni neutrals. Second, electronically excited species move faster than species in the ground state or lower lying states. Third, the TOF spectrum of Ni^* neutrals extending to about 200 ns is similar as a whole to that of $\text{Ni}^{+'}$ ions. Fourth, the TOF spectrum of Ni^* neutrals is also similar as a whole to that of O^* neutrals. However, there is a difference between these two spectra, that is, the second peak is larger than the first peak for O^* neutrals, whereas only a shoulder of the first peak is seen for Ni^* neutrals. Fifth, the TOF spectrum of Ni neutrals has a long tail extending to above $2 \mu\text{s}$. The tail length increases with θ . Almost all features mentioned above are also observed at $\theta = 15^\circ$, 30° , and 45° except for the disappearance of $\text{Ni}^{+'}$ ions at 30° and 45° and relative enhancement of slow components of Ni neutrals at larger θ .

In our experimental setup, species passing through a rectangular prism whose cross section is $25 \times 25 \mu\text{m}^2$ are detected. Even if this rectangular prism is located at point A, many species run more than 1 mm before they reach there, that is, only the species ejected normal to the surface run 1 mm, and the species ejected with an angle θ against the surface normal run $1/\cos \theta$ mm. Therefore, $\alpha(t)$ and $I(t)$ are not regarded as TOF spectra in the same sense as those in the mass spectroscopy where species coming into a narrow solid angle are detected. However, it would be at least plausible to take the first peak of $\alpha(t)$ or $I(t)$ as the most probable velocities for species running on the shortest way, if the velocities and densities of the species ejected normal to the surface is not smaller than those of the species ejected obliquely. The only exception is the case of $\theta = 45^\circ$ of Ni neutrals, because the first peak is smaller than the second peak.

The most probable velocity v_p is then determined as $1 \times 10^{-3}/t_p(\text{ms}^{-1})$ when $\alpha(t)$ or $I(t)$ has the first peak at $t_p(\text{s})$ after the peak of the laser pulse, because the observation points are located 1 mm apart from the laser spot. Figure 5 shows the angular dependence of v_p of $\text{Ni}^{+'}$ ions and Ni neutrals indicated by solid marks, and v_p of $\text{Ni}^{+'}$ ions and Ni^* neutrals indicated by open marks. Figures 5(a) and 5(b) are for the fluences of 5.1 and 2.5 J/cm^2 , respectively. At the fluence of 5.1 J/cm^2 , v_p of $\text{Ni}^{+'}$ ions and Ni neutrals depend on θ only slightly; v_p of $\text{Ni}^{+'}$ ions and Ni neutrals are almost 1.5×10^4 and $7 \times 10^3 \text{ m/s}$, respectively. The only exception is the case of $\theta = 45^\circ$ of $\text{Ni}^{+'}$ ions. On the other hand, v_p of $\text{Ni}^{+'}$ ions and Ni^* neutrals seem to depend on θ , however, the TOF spectrum of Ni^* neutrals is similar to that of $\text{Ni}^{+'}$ ions as seen in Fig. 4. When the laser fluence is near the ablation threshold, 2.5 J/cm^2 , $\text{Ni}^{+'}$ ions are not observed clearly and v_p of $\text{Ni}^{+'}$ ions are determined only at $\theta = 0^\circ$. v_p of Ni^* and Ni neutrals monotonically decrease with θ , although Ni neutrals are not observed clearly at $\theta = 45^\circ$.

FIG. 5. Angular dependence of the most probable velocities of Ni^{++} ions (○), Ni^{+} ions (●), Ni^* neutrals (□), and Ni neutrals (■). The laser fluence was 5.1 J/cm^2 in (a) and 2.5 J/cm^2 in (b).

IV. DISCUSSION

A. Plume expansion

Expansion process of a plume is revealed by the velocity and density distribution of Ni^{++} and Ni neutrals shown in Figs. 4 and 5. Ni^{++} ions move faster than Ni neutrals and the tail of the TOF spectrum of Ni neutrals is much longer than that of Ni^{++} ions. On the other hand, angular dependencies of the most probable velocities of both Ni^{++} ions and Ni neutrals are almost isotropic. This difference and similarity between Ni^{++} ions and Ni neutrals are explained as follows.

The needle-like white plasma produced during laser pulse irradiation is highly ionized. After the laser pulse terminates, the plasma diffuses into vacuum due to density gradient. This plume expanding from the white plasma is known to be a weakly ionized plasma,⁷ where number densities of electrons and ions are nearly equal. Because the mass of

electron is much smaller than the mass of ion, electrons diffuse faster than ions. Consequently, the skin of the plasma is not electrically neutral, but made up of a double layer consisting of an electron-rich layer and electron-depleted layer. An electric field is then built in this sheath, which decelerates electrons and accelerates ions. Electrons and ions then move together interacting by Coulomb force. This is so-called ambipolar diffusion. Even after the temperature of the plasma decreases and ions inside the plume are recombined with electrons, the sheath expands with the velocity obtained by the acceleration in the early stage of plasma expansion. If diffusion of electrons into vacuum is isotropic, the expansion of the sheath is expected to be isotropic. Therefore, ions move faster than neutrals and the velocity of ions does not depend on the angle θ . This is in fairly good agreement with the experimental results shown in Figs. 4 and 5.

On the other hand, neutrals are not accelerated by the electric field, so that they move slower than ions. The angular dependence of velocities of Ni neutrals is almost isotropic at the laser fluence of 5.1 J/cm^2 . As is discussed later in Sec. IV B, Ni^* neutrals are produced mainly by the recombination of Ni^{+} ions with electrons. If Ni neutrals constituting the first peak of the TOF spectrum are produced dominantly in this process at the early stage of plasma expansion, angular dependence of velocity of Ni neutrals can be almost isotropic. This angular dependence of velocities of Ni neutrals is different from that of neutrals observed in the plume from $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$.¹⁹ The anisotropic angular dependence of velocity of neutrals found there, was explained by collisional interaction and volume evaporation. The difference between the cases of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ and NiO may come from different laser fluence. In the former case, the observation was carried out at the fluence up to 1.2 J/cm^2 , and in our case, the fluence of irradiation was 5 J/cm^2 . As shown in Fig. 5(b), v_p of Ni neutrals at a weaker fluence of 2.5 J/cm^2 monotonically decreases with θ , which agrees with the case of $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. At this fluence, the mechanism dominating the velocity of Ni neutrals may be collisional interaction or volume evaporation as pointed out in Ref. 19.

B. Electronic excitation

Intensity of optical emission is determined from two factors; number density of species and electronic excitation process. Absorbance is determined mainly from the number density of species. Measurements of both emission intensity and absorbance thus provide information about the excitation process of species. The TOF spectra of Ni^{++} ions and Ni^* neutrals have peaks at 40 and 55 ns after the laser pulse, respectively. On the other hand, the lifetimes of the upper a^4D_2' state of Ni^{+} ion and $y^3G_5^o$ state of Ni neutral are 2.2 and 1.4 ns, respectively, as listed in Table I.²⁴ Therefore, the excited species are not produced in the highly ionized plasma at the early stage, but they are produced during the expansion of the plume.

It is noted in Fig. 4 that the TOF spectrum of Ni^* neutrals is similar to that of Ni^{++} ions. This feature is also observed at $\theta = 15^\circ$, 30° , and 45° . This suggests that the excitation probability of Ni neutrals is proportional to the density

of Ni^{++} ions. Consequently, it is natural to conclude that Ni^* neutrals are produced by the recombination of Ni^{++} ions with electrons. Moreover, the TOF spectrum of Ni^* neutrals is also similar to that of O^* neutrals. The lifetime of the upper $3p^5P$ states of O neutral is 29 ns, so that O^* neutrals are also produced during the expansion of the plume. The TOF spectrum of O^{++} ions is found to be quite similar to that of Ni^{++} ions at the laser fluence of 50 J/cm^2 , so that the TOF spectrum of O^+ ions is probably similar to that of Ni^+ ions even at the fluence of 5.1 J/cm^2 . Therefore, O^* neutrals are also supposed to be produced by the recombination of O^+ ions with electrons.

When ion temperature decreases below about 1 eV, Ni^{++} ions disappear, because Ni^{++} ions are in the lower lying states about 1 eV higher than the ground state. Therefore, even if Ni^{++} ions are not observed, Ni^+ ions may be observed, that is, the TOF spectrum of Ni^+ ions may have a longer tail than that of Ni^{++} ions. However, this is not likely for the following reasons. If electron temperature as well as ion temperature decreases below about 1 eV, the recombination of Ni^+ ions with electrons is expected to increase significantly, because, in general, the coefficient of three body recombination drastically increases when the electron temperature decreases below 1 eV.²⁹ The increase of the recombination causes the increase of the number density of Ni^* neutrals. Then, the TOF spectrum of Ni^* neutrals would have a longer tail than that of Ni^{++} ions, if significant number of Ni^+ ions ran after Ni^{++} ions. This is not consistent with the results in Fig. 4. This means that the TOF spectrum of Ni^{++} ions is approximately equal to the number density of Ni^+ ions. This confirms the above conclusion that the recombination of Ni^+ ions with electrons is the dominant process to generate Ni^* neutrals.

It is noted in Fig. 5 that Ni^{++} ions are observed even at $\theta = 45^\circ$, whereas Ni^{++} ions are only observed at $\theta = 0^\circ$ and 15° . This means that only Ni^+ ions ejected nearly normal to the surface are excited to higher states. One possible explanation for this angular distribution of Ni^{++} ions is that the density of electrons emitted normal to the surface is higher than that of electrons emitted obliquely. Higher density of forward emitted electrons can be attributed to thermal electron emission at the very early stage of ablation which is oriented to the surface normal. However, this is not likely because this leads to anisotropic electron diffusion and then anisotropic ion diffusion, which disagrees with the observed results in Fig. 5. The other possibility is that the multiple collisional effect yields an angular distribution of the number density of species like $\cos^n \theta$.³ This effect may produce excited ions preferentially in the forward direction.

C. Species ejection

The TOF spectrum of Ni^* neutrals is similar to that of O^* neutrals. If these TOF spectra of excited neutrals represent the onsets of TOF spectra of neutrals in the ground state, the fast component of the TOF spectrum of O neutrals is probably similar to that of Ni neutrals. This similarity means that Ni and O atoms are generated mainly by the dissociation of NiO molecules after they leave the target surface, that is,

ejection of species as NiO molecules or clusters are the dominant process, but evaporation as Ni or O neutrals is a minor process. This interpretation is in accord with the generally accepted mechanism of laser ablation.³

On the other hand, the long tail of TOF for Ni neutrals may be explained by thermal evaporation continuing for some time after the laser pulse terminates due to high surface temperature. Thermal evaporation of the energy of less than 1 eV does not produce many ions, so that, the tail of the TOF spectrum is not expected to be long for Ni^+ ions. As θ increases, the tail of the TOF spectrum becomes relatively larger compared with the first peak. This means that the tail has a rather weaker angular dependence than the fast component. Therefore, the angular distribution of the number density of the fast component is expected to be like $\cos^n \theta$ ($n > 1$), because that of the thermally ejected species is like $\cos \theta$.

V. SUMMARY

The structure of the plume induced by the laser ablation of NiO in vacuum and its evolution has been studied. TOF spectra of various species and their angular dependencies were determined from the temporally resolved optical absorption and optical emission spectra and their angular dependence.

Notable findings at the optimum laser fluence for pulsed laser deposition (5.1 J/cm^2) are as follows: Ni^+ ions move faster than Ni neutrals. Electronically excited species move faster than species in the ground state or lower lying states. Ni^{++} ions are detected only at $\theta = 0^\circ$ and 15° . The TOF spectrum of Ni^* neutrals is similar as a whole to that of Ni^{++} and O^* neutrals. The most probable velocities of Ni^{++} and Ni are only slightly dependent on the ejection angle. The TOF spectrum of Ni neutrals has a long tail whose length increases with θ .

Evolution of the plume induced by the laser ablation of NiO in vacuum is revealed from the present results. Most of the species are initially ejected as NiO molecules or clusters, and dissociated into Ni and O species in the plume. Ni^+ ions are accelerated by the electric field within the sheath of the plume. This ambipolar diffusion yields isotropic angular dependence of velocities of ions and neutrals. Ni^* neutrals are mainly generated by the recombination of Ni^+ ions with electrons in the sheath of the plume. Ni^+ ions are ejected even at $\theta = 45^\circ$, but Ni^{++} ions are produced at nearly $\theta = 0^\circ$, which may be due to the multiple collisional effect. The long tail of the TOF spectrum of Ni neutrals corresponds to thermal evaporation.

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