JOURNAL OF MATERIALS SCIENCE **35** (2000) 1469–1474

Ion probe measurement of Fe species ejected by KrF laser ablation of Fe in ambient nitrogen gas

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Time-resolved ion current measurements for laser ablation of Fe in nitrogen gas were performed. The current due to electrons, N_2^+, Fe ion and Fe neutral was observed at the substrate. At nitrogen pressures between 1×10^{-3} Torr and 1×10^{-1} Torr, the amount and the velocity of the Fe ion arriving at the substrate increased as the nitrogen pressure was increased. The velocity of the Fe ion was approximately 60 km/s and the maximum amount of it was estimated to be not more than 0.3 percent of the ejected Fe species. The Fe-N thin films prepared in this nitrogen pressure region showed the highest (200) orientation and increase of the crystallite size. It is considered that the Fe ion arriving at the substrate has the effect of enhancing the mobility of deposited species, resulting in the generation of the highest oriented Fe-N thin film composed of the largest crystallites.

1. Introduction

Ferromagnetic iron nitride compounds have attracted considerable attention recently as possible materials for applications as magnetic recording heads and magnetic recording media. This interest is due to the large saturation magnetization, good corrosion resistance and good mechanical properties of iron nitride compounds [1]. It has been demonstrated that saturation magnetization can be larger than bulk iron for low nitrogen contents [2].

Pulsed laser deposition is a promising technique for the preparation of high quality films with adatom energy. The high energy species ejected from a target excite reactive ambient gas such as nitrogen and arrive at a substrate with plasma formation. As a result, high quality films can be grown at a lower substrate temperature as compared to other methods such as sputtering [3], and metastable materials such as c-BN [4] can be obtained. While the pulsed laser deposition is adopted for the preparation of many kinds of thin films including oxide [5], semiconductor [6] and metal [7], studies on elemental processes responsible for the ablation and film deposition are under way, and the relation between the deposition process and the properties of the resulting films have not been elucidated yet. In various deposition techniques, the bombardment of the energetic particles, in particular energetic ions, during the film deposition is known to enhance the film growth, including density, grain size, and crystallographic orientation [8]. Thus, the same effects of the energetic particles are expected for pulsed laser deposition, but they are as yet unknown.

For the characterization of ablated fragments as deposits, many spectroscopic techniques have been used, including optical spectroscopy [9], ion probe [10], laser-induced fluorescence [11], and mass spectroscopy [12]. In a previous study [13, 14], a framing streak camera was employed to obtain an insight into laser-ablated iron plume propagation in a background of nitrogen, and a time-resolved emission spectrum analyzer was applied to determine the excited species in the ablation plume. It was found that most of species ejected from the Fe target consist of Fe neutrals, which are divided into two groups with different velocities of 2×10^4 m/s and 1×10^4 m/s. In an emission measurement, however, it is impossible to observe non-emission species and weakly emitting species such as Fe ions. As a consequence, the relation between the deposition process and the properties of the resulting films have not been elucidated yet. In order to make it clear, ion probe measurement was applied in this study. In this paper, I report the result of a study in which I investigated the relation between the ablation process and the microstructure of deposited films.

2. Experimental

The experimental setup of the ion current measurement is shown in Fig. 1. A KrF excimer laser [248 nm wavelength] was focused onto the iron target (99.9%) at an angle of 70° to the target normal (2 mm × 3 mm image on the target surface). The fluence, which was evaluated by a burn pattern on a Polaroid film and the laser energy measured inside the chamber, was 3.2 J/cm^2. The full-width at half-maximum of the laser pulse was 27 ns and the repetition rate used was 10 Hz. The chamber was evacuated to a base pressure under 10^{-8} Torr using a cryopump, and the background nitrogen pressure was

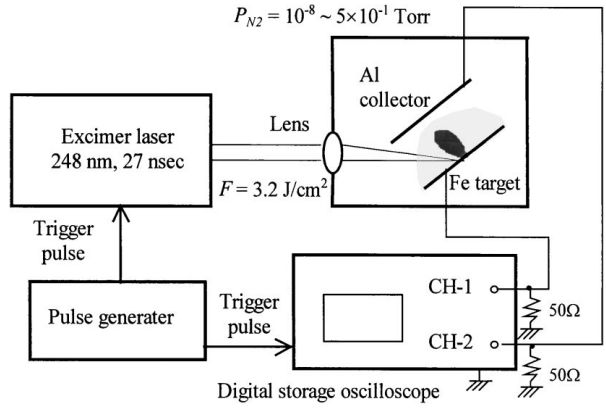

Figure 1 Experiment apparatus for ion probe measurement.

maintained between 10^{-8} Torr and 5×10^{-1} Torr adjusting the input of nitrogen gas. The current from the Al collector (30 mm × 40 mm) at a distance of 30 mm from the Fe target into the ground and the current from the Fe target into the ground were measured simultaneously using a digital storage oscilloscope with two channels. The position of the Al collector was set at the same position as the substrate for depositing Fe-N thin films. The currents observed at the Al collector are composed of the positive current and the negative one. The former is due to positive ions arriving at the Al collector and due to secondary electrons ejected from the Al collector by the bombardment of the Fe neutrals with high energy. The latter is due to thermal electrons ejected from the Fe target by laser irradiation. The excimer laser and the digital storage oscilloscope were triggered using a pulse generator with two outputs. The time when the current due to thermal electrons starts to flow at the Fe target was defined as the time $t = 0$, because it takes negligible time, which is less than few nanoseconds [15], for thermal electrons to be ejected from the Fe target after the laser irradiation on the Fe target.

Fe-N thin films 200–500 nm thick were deposited on glass substrates set at a distance of 30 mm from the Fe target. The repetition rate of the laser pulses was 10 Hz. The deposited film thickness per pulse was 0.025 nm and the deposition rate was 0.25 nm/s. The substrate temperature was 20–250°C. The crystallite structure of the deposited films was studied by an X-ray diffraction (XRD) method using Cu-K_α radiation. The identification of the generated Fe-N phases was made using the results of XRD and magnetic property measurements [16].

3. Results and discussion

Typical current signals observed at the Fe target and at the Al collector are shown in Fig. 2. Since the thermal electrons ejected from the Fe target take less than 50 ns to arrive at the Al collector [13], the lag time between the ejection from the Fe target and the arrival at the Al collector can be neglected. The positive current at the Fe target was observed at $t = 0$–2.5 μs. This indicates that the thermal electrons eject from the Fe target by laser irradiation [15].

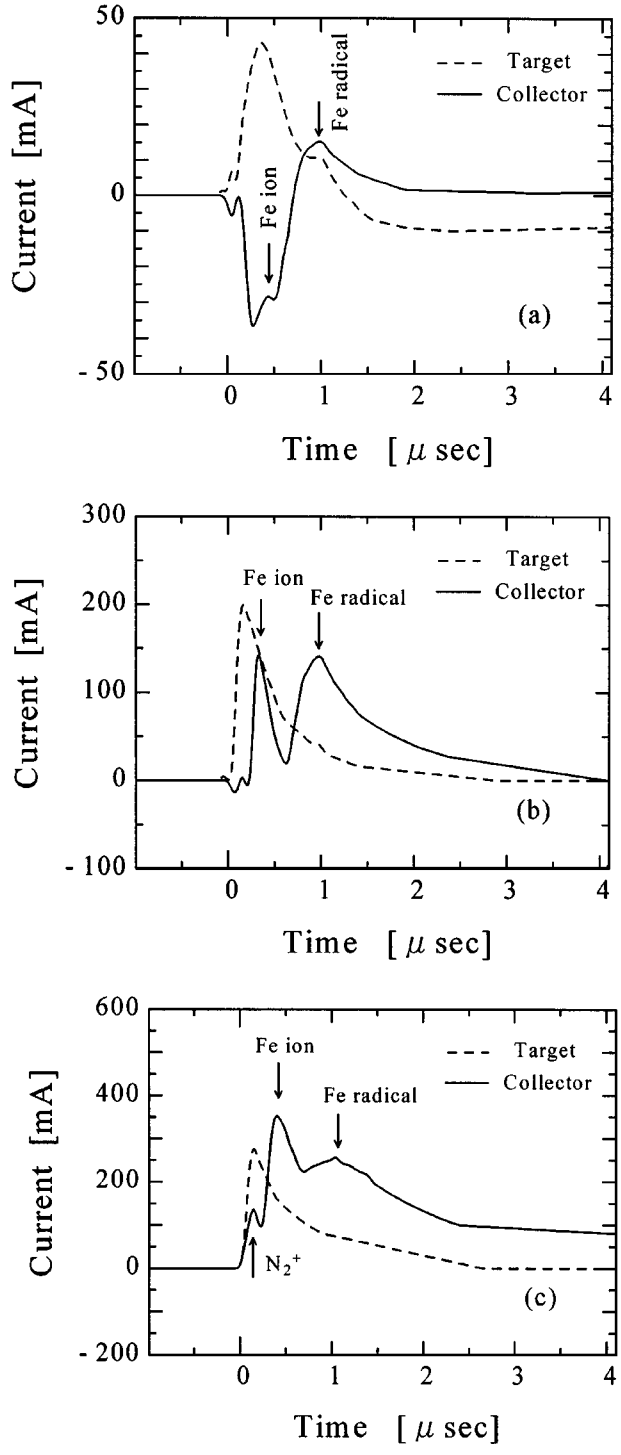

Figure 2 The current signal at the Fe target (dashed line) and the one at the Al collector (solid line). (a) 5×10^{-4} Torr, (b) 5×10^{-2} Torr.

In a previous paper [13], I reported that the thermal electrons ejected from the Fe target collide with nitrogen molecules in the atmosphere resulting in the generation of the hemispherical plume due to N_2^+ emission. These thermal electrons are included in the current measured at the Al collector. The thermal electrons are ejected according to the cosine law. Using this, the amount of electrons arriving at the Al collector can be estimated to be approximately 60 percent for the whole flux of electrons ejected from the Fe target. It is thought that the signal, which is inverted and reduced by 60 percent from the current measured at the Fe target, is included in the collector signal. Thus, the Al

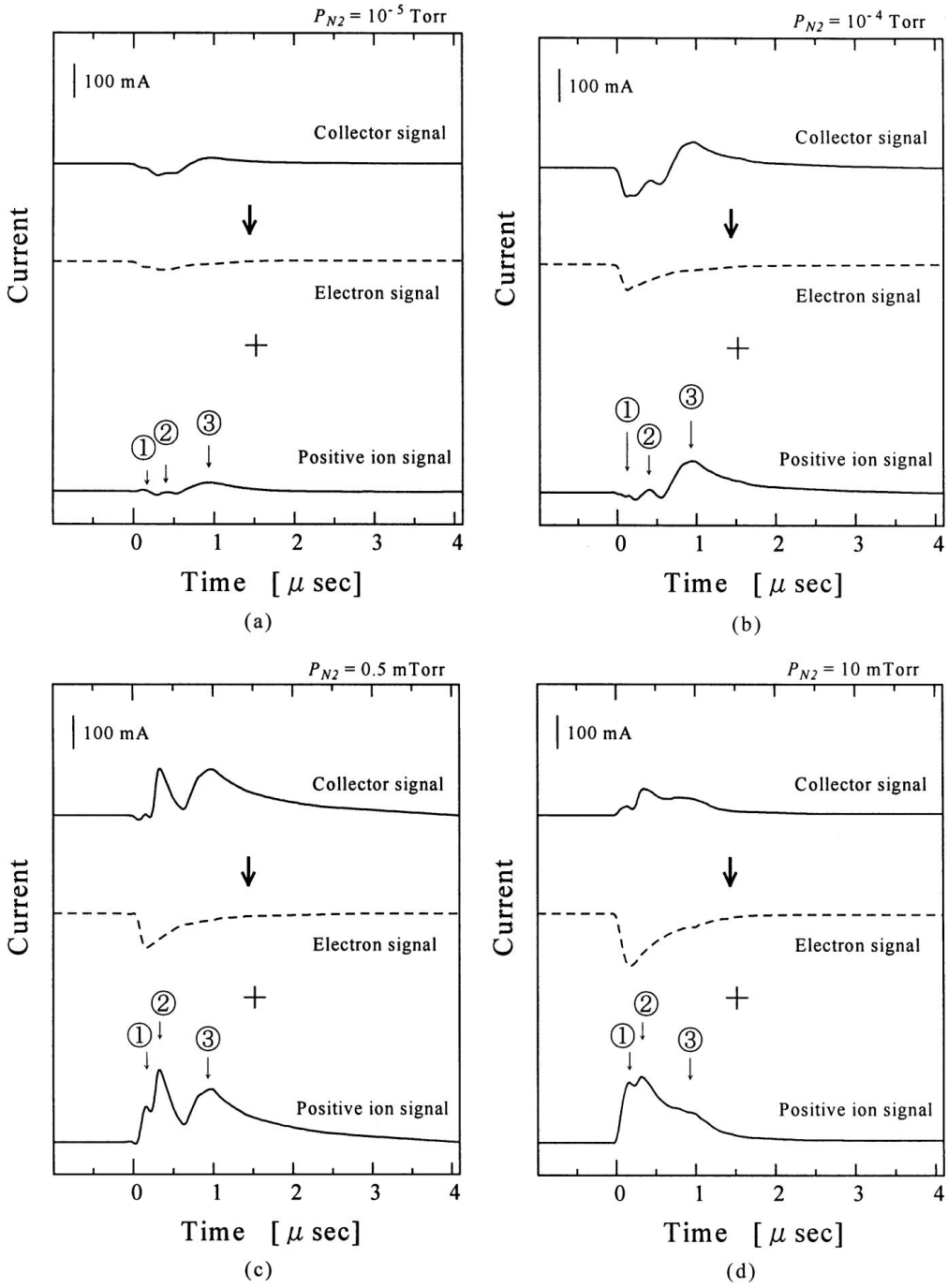

Figure 3 The separation of the current signal observed at the Al collector into the thermal electron signal and the positive ion signal with three peaks (①: N_2^+, ②: Fe ion, ③: Fe neutral). (a) 5×10^{-4} Torr, (b) 1×10^{-2} Torr.

collector current can be roughly separated into two elements. One is due to the thermal electrons, and the other is due to the Fe ions, Fe neutrals etc. as shown in Fig. 3. In the positive ion signal the first peak coincides with the N_2^+ emission observed in the previous study using a time-resolved emission spectrum measurement [14]. Thus, the first peak is thought to be due to arrival of N_2^+ at the Al collector. The species consisting of the third peak have a mean velocity of around 20 km/s, which can be estimated using the peak position and the distance between the target and the Al collector. This velocity is nearly same as that of the fast Fe neutrals observed in the emission spectroscopy [14]. Thus, the third peak is thought to be due to arrival of the fast Fe neutrals. On the other hand, emission lines corresponding to the second peak have not been observed in the emission spectroscopy [14]. The position of the second peak was shifted for the amount of the electrons ejected from the target, as described below. In other words, the species consisting the second peak were accelerated by the coulomb field. Therefore, it is thought that the second peak is due to Fe ions. Emission lines due to Fe ions could not be observed in the emission spectroscopy. This might be because the intensities of Fe ion emissions are small compared with that of Fe neutral emissions in general and the fraction of the Fe ion in emission species is extremely small.

The peak current of the first, second and third peaks are shown in Fig. 4, respectively. The current of the first

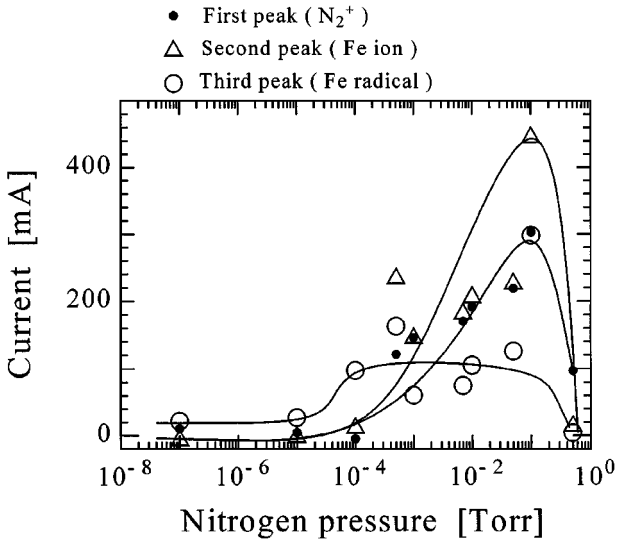

Figure 4 Dependence of the peak current of the first peak (•: N_2^+), the second peak (Δ: Fe ion) and the third peak (O: Fe neutral) on the nitrogen pressure.

peak, which is due to N_2^+, increases as nitrogen pressure rises at more than 10^{-3} Torr. The mean free path is approximately 5 cm, which is comparable with the distance between target and Al collector, at a nitrogen pressure of 10^{-3} Torr, and it decreases as the nitrogen pressure increases. The increase of the N_2^+ current corresponds to the increase of the collisions between the electrons ejected from the Fe target and N_2 in atmosphere. Thus, the excitation from N_2 to N_2^+ is attributed to the collisions between the electrons and the N_2.

There is the overlapping time between the arrival of N_2^+ and that of Fe ions at the Al collector, which was set at the same position as the substrate in the Fe-N film deposition. Hence, it is expected that N_2^+ ions react with the Fe ions resulting in the growth of Fe-N thin film at the substrate. The number of N_2^+ arriving at the collector for a laser pulse could be estimated to be 10^{-12} at most at a nitrogen pressure of 10^{-1} Torr, by integrating the current of the first peak. The number of the Fe atoms arriving on the substrate for a laser pulse could be also estimated to be about 5×10^{14}, using the film volume calculated from the film thickness. This estimation was under the assumption that the film consists of dense crystallites with bcc Fe lattices. The ratio between the number of N_2^+ and that of the Fe for a laser pulse is extremely small (0.2 percent). Thus, it is considered that N_2^+ hardly contributes to the nitridation of deposited films. Therefore, the nitridation of the deposited films occurs predominantly after the deposition of species. In other words, it occurs between the deposited species and ambient N_2 using the internal energy of deposited species on the film surface during the interval between laser pulses [14].

It is known that the ion probe measurement of the pulsed laser ablation shows a positive current at a collector due to the secondly electron emission caused by bombardment of high energy neutral species on the collector [17, 18]. The Fe neutrals composing of the third peak have an energy of more than 140 eV, which is estimated from the mean velocity between the Fe target and the Al collector assuming the Fe neutrals are atomic. This estimated energy exceeds by far the threshold of the secondary electron emission, which is a few electron volts. Thus, positive current due to arrival of Fe neutrals was observed at the Al collector in spite of Fe neutral being not charged.

The Fe ion current composing of the second peak increases at a nitrogen pressure of more than 10^{-3} Torr and has a maximum of 450 mA at 10^{-1} Torr. The change of the current peak corresponds to that of total ion charges, since the shape of current signals hardly depend on the nitrogen pressure. The total ion charges of the second peak at 10^{-1} Torr was calculated to be 2.4×10^{-7} C. Using this value, the number of the Fe ions can be estimated to be 1.4×10^{12} on the assumption that the Fe ions are single charged. The number of the Fe atoms deposited on the substrate for a laser pulse is estimated to be about 5×10^{14} from the film volume. Therefore, it was found that the ratio between the number of Fe ion arriving at the substrate and that of Fe atoms deposited on the substrate is no more than 0.3 percent. It has been reported that ion bombardment during film growth has the effects of enhancing film growth including density, grain size and crystallographic orientation in various deposition techniques. This effect is expected for the Fe-N deposition by the pulsed laser ablation at nitrogen pressure between 10^{-3} Torr and 10^{-1} Torr, at which the number of the Fe ion increases. In fact, the prepared Fe-N thin films show highly (200) or (002) orientation of the α^* phase [16, 19], and the $\Delta\theta_{50}$, which indicates the degree of the orientation, has a minimum of about 5° at the 2×10^{-3} Torr as shown in Fig. 5a. In addition, the crystallite diameter in depth direction estimated using Scherrer formula increases at a nitrogen pressure between 10^{-2} Torr and 5×10^{-2} Torr as shown in Fig. 5b. These must be mainly due to the bombardment of the Fe ions. But it is not clear which of these are dependent on the number of Fe ion in a unit time or the total number of Fe ion. At more than 10^{-1} Torr, all currents due to N_2^+, Fe neutral and Fe ion decrease critically as the nitrogen pressure rises. This is because the species ejected from the target are highly scattered by the ambient nitrogen molecules.

The positive current at the Fe target, which is due to the ejection of the thermal electrons, depends on the nitrogen pressure. The change with nitrogen pressure is shown in Fig. 6. Also the arrival time of the Fe ions and neutrals at the Al collector depends on the nitrogen pressure. Dependence of them and the mean velocity estimated using them on the nitrogen pressure are shown Fig. 7a and b, respectively. The current due to thermal electron ejection increases critically as the nitrogen pressure rises above more than 10^{-4} Torr, as shown in Fig. 7. The arrival time of the Fe ion decreases in accordance with the increase of the thermal electron current measured at the Fe target, as shown in Fig. 6. Since the thermal electrons arrive at the Al collector earlier than the Fe ion, it can be considered that the Fe ions are accelerated by the electric field induced by the ejected thermal electrons. The Fe neutrals composing the third peak are also accelerated

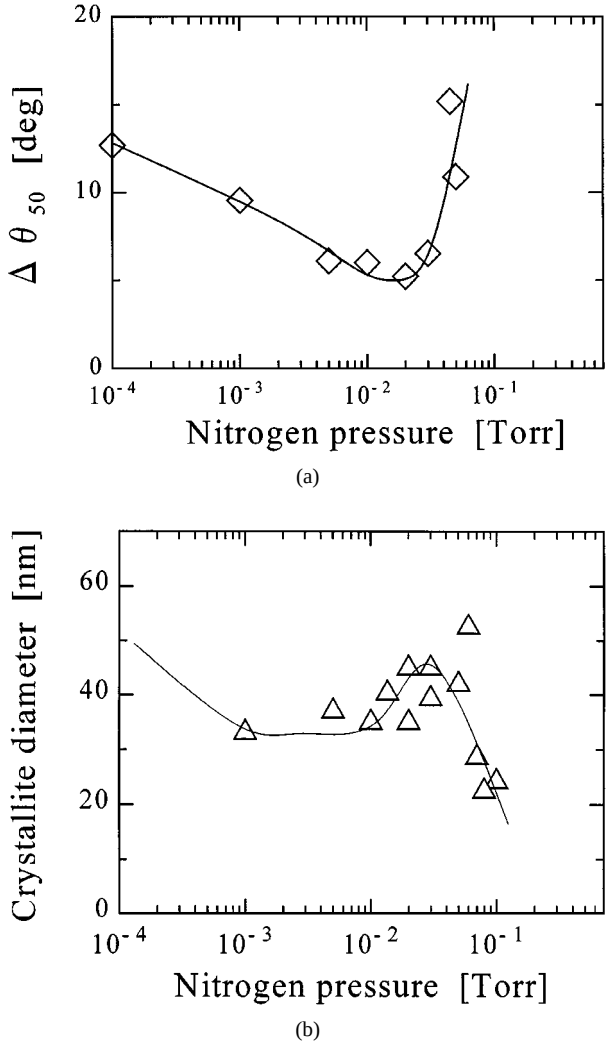

Figure 5 Dependence of (a) the $\Delta\theta_{50}$ of the α^* (002) or (200) peak and (b) the crystallite diameter estimated using the Scherrer formula on the nitrogen pressure.

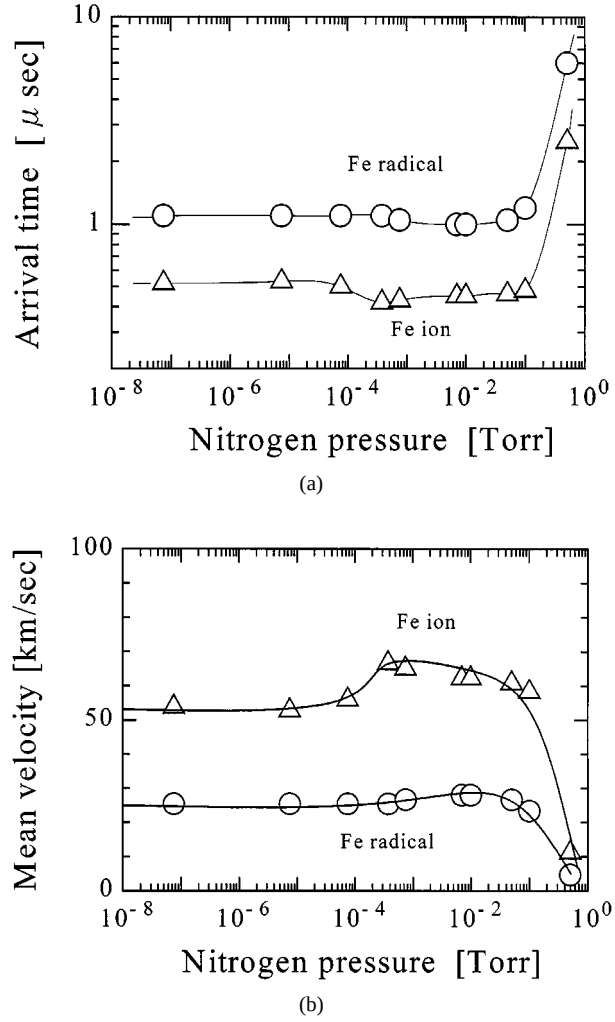

Figure 7 Dependence of (a) the arrival time of the Fe ion (△) and the Fe neutral (○) at the Al collector, and (b) the mean velocities of the Fe ion (△) and the Fe neutral (○), on the nitrogen pressure.

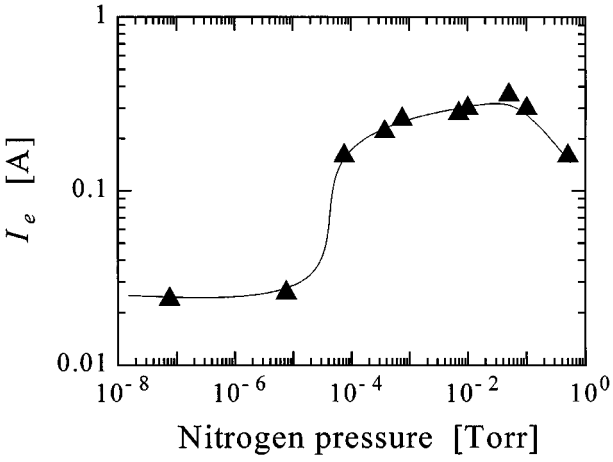

Figure 6 Dependence of the peak current observed at the Fe target due to the thermal electron ejection from the Fe target on the nitrogen pressure.

slightly in this pressure range. The emission spectrum measurement showed the continuous spectrum due to Bremsstrahlung emission, and thus, the ejected species construct the hot plasma near the target surface. Therefore, Fe neutrals observed at the Al collector might be charged at the beginning of the ejection from the target. Consequently the third peak is shifted for the amount of the electron ejected from the target.

The mean velocity of the Fe ion was estimated to be 60 km/s at less than 10^{-4} Torr, while it increases to approximately 60 km/s in the nitrogen pressure region between 10^{-3} Torr and 10^{-1} Torr. On the assumption that Fe ion is atomic, the kinetic energy of the Fe ion was estimated to be 810 eV for nitrogen pressure of less than 10^{-4} Torr and to be approximately 1000 eV for the pressure region between 10^{-3} Torr and 10^{-1} Torr. The mean velocity of the Fe neutral was hardly dependent on the nitrogen pressure at less than 10^{-1} Torr and was estimated to be 24 km/s. This value is in agreement with that of the fast Fe neutral observed in the time-resolved emission measurement [14] and that of the front edge of the expanding plume observed using a framing streak camera [13]. The kinetic energy of the Fe neutral was estimated to be 170 eV on the assumption that they are atomic. At more than 10^{-1} Torr, both arrival time of the Fe ion and the Fe neutral are considerably delayed as the nitrogen pressure rises. This is because the species ejected from the target were highly scattered by ambient nitrogen molecules.

4. Conclusion

Ion probe measurement for laser ablation of Fe in a nitrogen atmosphere was made in order to investigate the relation between the film growth and the ablation process. The currents due to N_2^+, Fe ion and Fe neutral were observed at the Al collector, which was set at the same position as the substrate. The mean velocities of the Fe ion and Fe neutral were estimated to be 53 km/s and 23 km/s, respectively. These were not dependent on nitrogen pressure at less than 10^{-3} Torr. At nitrogen pressures between 10^{-3} Torr and 10^{-1} Torr, the Fe ions were accelerated by the electric field caused by the electrons ejected from the target. As a result, its mean velocity increased and got to be 60 km/s. In addition, the amount of arrival of Fe ion at the Al collector increases in this pressure region. The ratio of the Fe ions for the whole Fe species deposited on the substrate was estimated to be 0.3 percent at most. The deposited Fe-N films deposited in this pressure region showed the highest orientation and largest crystallite size. This enhancement of the film growth must be attributed to the bombardment of energetic Fe ions as well as other preparation methods. At more than 10^{-1} Torr, the velocity of the Fe ion and neutral decreases critically as the nitrogen pressure rises. Simultaneously the amount of them also decreases. According to their decreases, the deposited films showed the reduction of crystal orientation and crystallite size. The arrival time of N_2^+ at the Al collector has the overlapping with that of the Fe ion. Thus, the Fe ions are expected to react with N_2^+. But the amount of N_2^+ is extremely small compared to that of Fe deposited on the substrate. Therefore, the N_2^+ hardly contribute to the nitridation of deposited films. It is thought that the nitridation of the deposited films occur predominantly between the deposited species and ambient N_2 using the internal energy of deposited species on the film surface during the interval between laser pulses.

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Received 12 February 1998
and accepted 30 September 1999