Effect of hot filament on preparation of YBCO superconducting films by pulsed laser ablation in nitrous oxide gas

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Abstract

$YBa_2Cu_3O_x$ (YBCO) films were prepared in nitrous oxide (N_2O) gas by pulsed laser ablation (PLA) using Kanthal hot filament of about 1000 °C for cracking the N_2O gas. The crystal orientation was changed from a-axis to c-axis by turning-on the filament. The possible origin of this result is a rise of surface temperature of the substrate by thermal radiation from the hot filament and/or generation of oxygen-related radicals produced by cracking of N_2O. Temperature measurements revealed that the change of crystal orientation caused by the hot filament could be partly explained by the substrate heating effect. Mass-analysis revealed that N_2O gas was really cracked by the hot filament, supporting the possible change of the crystal orientation by the cracking effect of N_2O.

Keywords List

YBCO thin films, PLD, Hot filament, Nitrous oxide

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1. Introduction

For growth of high-quality oxide films, e.g., ferroelectric, ferromagnetic, and superconducting films, on various substrates at low substrate temperatures, the effects of ambient gas in various growth techniques have been studied using oxygen (O_2) [1], nitrous oxide (N_2O) [1], ozone gases (O_3)[2], and so on. In the present study, oxide films were prepared in N_2O ambient gas by pulsed laser ablation (PLA) using a hot filament. So far, the hot-filament technique has been employed mainly for film growth of diamond [3], silicon and silicon based-films [4] because of the efficient cracking of hydrogen and the related gases. The nitridation of gallium arsenide was also reported using nitrogen through a hot filament [5]. On the contrary, it seems to be difficult to crack oxygen related gases because of the oxidation damage of the filament. Tungsten filaments are easily degraded by oxygen because of the formation of volatile tungsten oxide. There has been no report on oxide film growth using the thermal cracking of oxidizing gases by a hot filament. However, the addition of a small amount of O_2 into the diamond deposition process using a hot filament has been reported [6]. Thus, we propose Kanthal wire as a filament for cracking oxidizing gases. Kanthal is known to be an oxidation-resistant alloy consisting mainly of iron, chromium, and aluminum.

In the present study, instead of O_2, N_2O was adapted because of the low decomposition temperature. N_2O is a linear molecule and resonates between N= N= O and N≡N –O. The expected reactions of N_2O gas by certain excitations are as follows:

$$2N_2O \rightarrow 2N_2 + 2O$$
$$2N_2 + 2O \rightarrow 2N_2 + O_2 \qquad (1)$$
$$2N_2O \rightarrow 2NO + 2N$$
$$2NO + 2N \rightarrow 2NO + N_2 \qquad (2)$$

2. Experimental

YBCO films were prepared by PLA with and without the presence of a hot (about 1000 °C) Kanthal as illustrated in Fig.1. Film preparation condition is summarized in Table I. For observing cracked fragments a quadrupole mass analyzer was attached to the deposition chamber.

Before using the Kanthal filament, it is fully oxidized for 5 min by turning it on in atmospheric air for stabilization. The change in the surface composition obtained by electron-probe microanalysis (EPMA) is shown in Table II. A surface segregation of Al_2O_3 after running of the filament in air for 5 min is clearly confirmed. The data in the right column will be discussed later.

3. Results and discussion

Figure 2 shows the XRD patterns for YBCO films prepared with and without the hot filament. YBCO films with the a-axis orientation were grown at the substrate temperature of 620 °C without the hot filament. When the filament was turned on, the crystal orientation was changed from the a-axis to the c-axis. The possible origin of this result is a rise of surface temperature of the substrate by thermal radiation from the hot filament or the generation of oxygen-related radicals as a result of the cracking of N_2O. A similar enhancement of crystal growth was reported for $Pb(Zr_{0.52}Ti_{0.48})O_3$ films by using an electron- emitting filament with a negative bias of –20 V[7]. It should be noted that there was no biasing in the present experiment for avoiding generation of energetic ions.

First, to examine the former possibility, the surface temperature of the MgO substrate was measured by a thermocouple and an infrared radiation thermometer. The temperature was found to be increased by 20 to 40 °C due to the hot filament.

YBCO films with the c-axis orientation were also obtained in N_2O gas by increasing the substrate temperature by about 50 °C without the hot filament, as shown in Fig.3. Figure 4 shows a comparison between the results of Fig.2 and Fig.3. In Fig.4 the ratio of the (005) to the (006) diffraction intensity I(005)/I(006) of YBCO films as a function of the substrate temperature is summarized. The horizontal dotted line represents the value for the film prepared with the hot filament at a substrate temperature of 620 ^{0}C. Based on these results, the change of crystal orientation caused by the hot filament could be partly explained by the substrate heating effect. For the film prepared at 620 ^{0}C without the hot filament, the ratio is evaluated by using the (200) intensity instead of the (006) intensity.

Second, to examine the latter possibility, the observation of N_2O cracking by the hot filament was performed by using a quadrupole mass analyzer without a built-in ionization filament. The result is shown in Fig. 5. All peaks observed in the mass spectrum were identified as peaks caused

by the source molecule of N_2O^+, and the cracked fragments of N_2^{2+}, O_2^{2+}, N_2^+, and NO^+. The fragments of m/e=14 and 16 can be identified as N^+ and O^+ as well, respectively.

Figure 6 shows the N_2O flow rate dependence of the respective mass peak intensities with the hot filament. Except for the mass intensity of the N_2O source gas, the intensities of almost all fragments are proportional to the flow rate, indicating there was no contamination in this experiment. These results indicate that N_2O gas was really cracked by the hot filament, supporting the possible change of the crystal orientation by the cracking effect of N_2O.

The stability of the Kanthal filament is, however, not sufficient for the long-term operation of cracking. Figure 7 shows the time dependence of intensities of the respective mass peaks. The intensities of N_2^+, $N_2^{2+}(N^+)$, and $O_2^{2+}(O^+)$ are almost constant, while N_2O^+ and NO^+ are decreasing with time. This degradation of the filament may be an origin of the small hot-filament effect in the film preparation.

For clarifying the origin of the filament degradation, the filament was inspected by scanning electron microscopy (SEM) and EPMA before and after running of the filament. As shown in Fig.8, running of the filament in N_2O degrades the filament surface significantly, resulting in surface roughening and final fracture of the filament. The serious surface degradation was not seen after running in atmospheric air. Furthermore, as seen from the Table II, the Al content on the filament surface is decreased after running in N_2O, supporting the above filament degradation. Kanthal wire is known to be oxidation resistant and very stable in atmospheric air. But it is found that the filament is not so stable in the present N_2O environment. For comparison, the filament was also examined in O_2 gas and a vacuum. The filament was broken in vacuum operation, indicating its instability in vacuum, while it was stable in O_2 gas. These results suggest that the instability of the Kanthal filament in N_2O is probably caused by the insufficient oxidation environment of N_2O.

For obtaining the best results regarding enhancing the crystal growth by cracking the oxidizing gas, it is necessary to increase the cracking efficiency in order to distinguish the cracking effect from the substrate heating effect, and also to employ a more stable filament in various oxidation environments.

4. Conclusion

When the filament was turned on, the YBCO crystal orientation was changed from the a-axis to the c-axis one. The possible origin of this result is a rise of surface temperature of the substrate by thermal radiation from the hot filament and/or generation of oxygen-related radicals produced by the cracking of N_2O.

5. Acknowledgements

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Table I. Film preparation condition

laser	Nd^{3+}:YAG
pulse width	7 ns
wavelength	532 nm
fluence	2.6 J/cm^2
repetition	2 Hz
substrate	(100)MgO annealed in O_2 at 1000 ℃
substrate temperature	620 ℃
deposition period	60 min
deposition environment	N_2O 40 Pa
sample cooling	5 deg/min in 100 hPa O_2

Table II. Change in the surface composition of Kanthal wire

	0 min	5 min in air	120 min in N_2O
Al	5.81 %	54.71 %	44.57 %
Cr	22.18 %	11.57 %	12.09 %
Fe	71.90 %	33.72 %	43.34 %

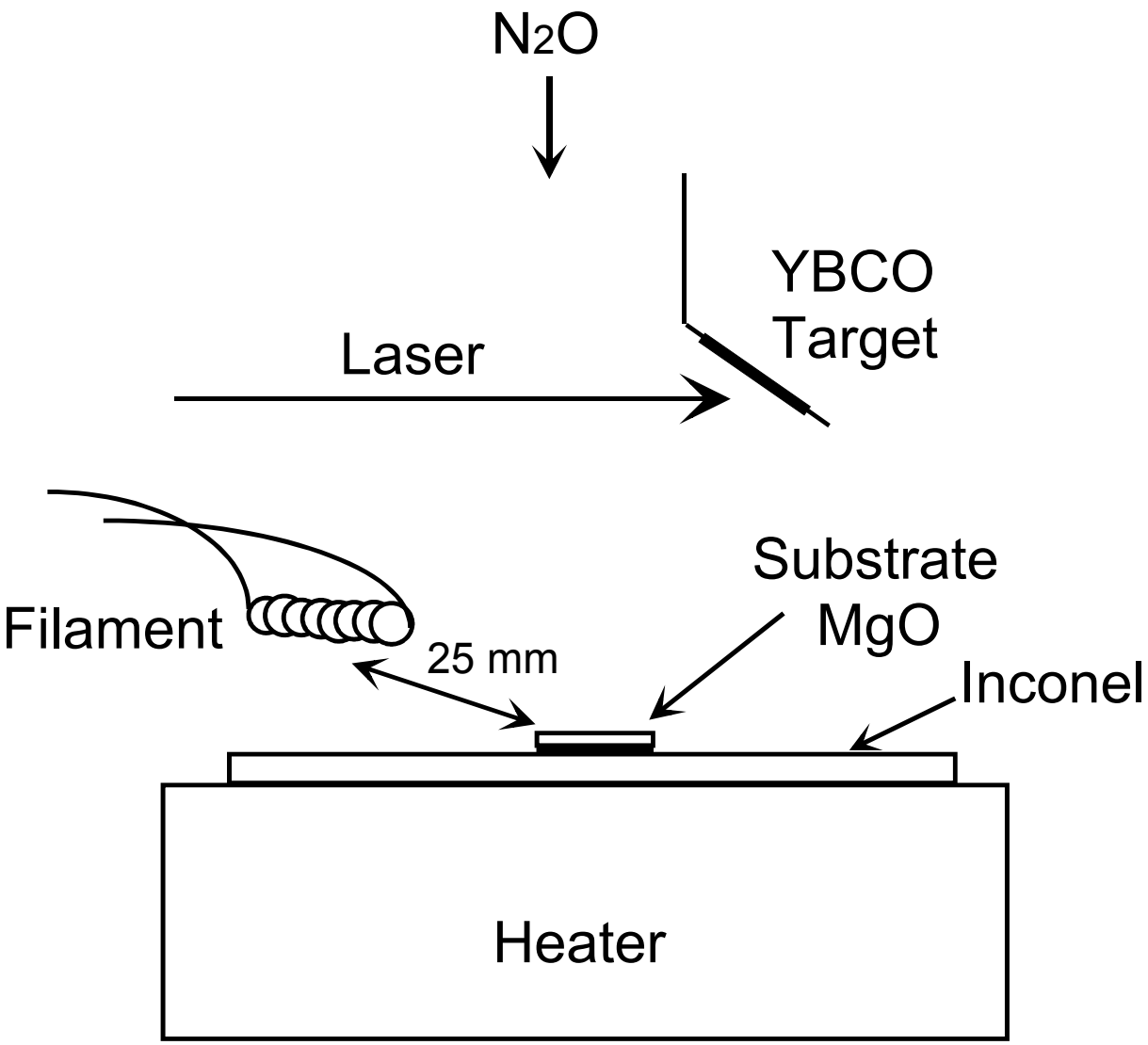


Fig.1 Schematic diagram of film preparation.

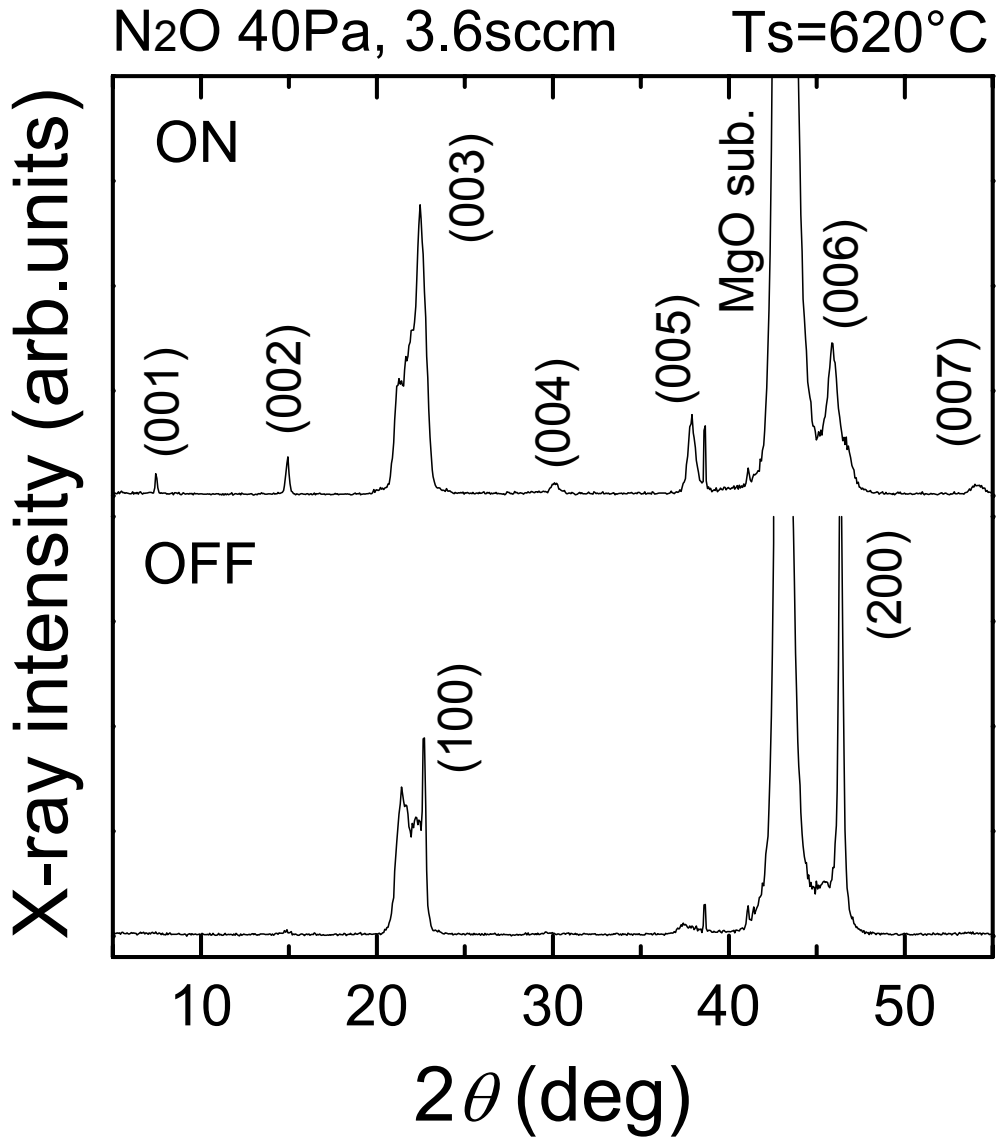


Fig. 2 XRD patterns for YBCO films prepared with and without the hot filament.

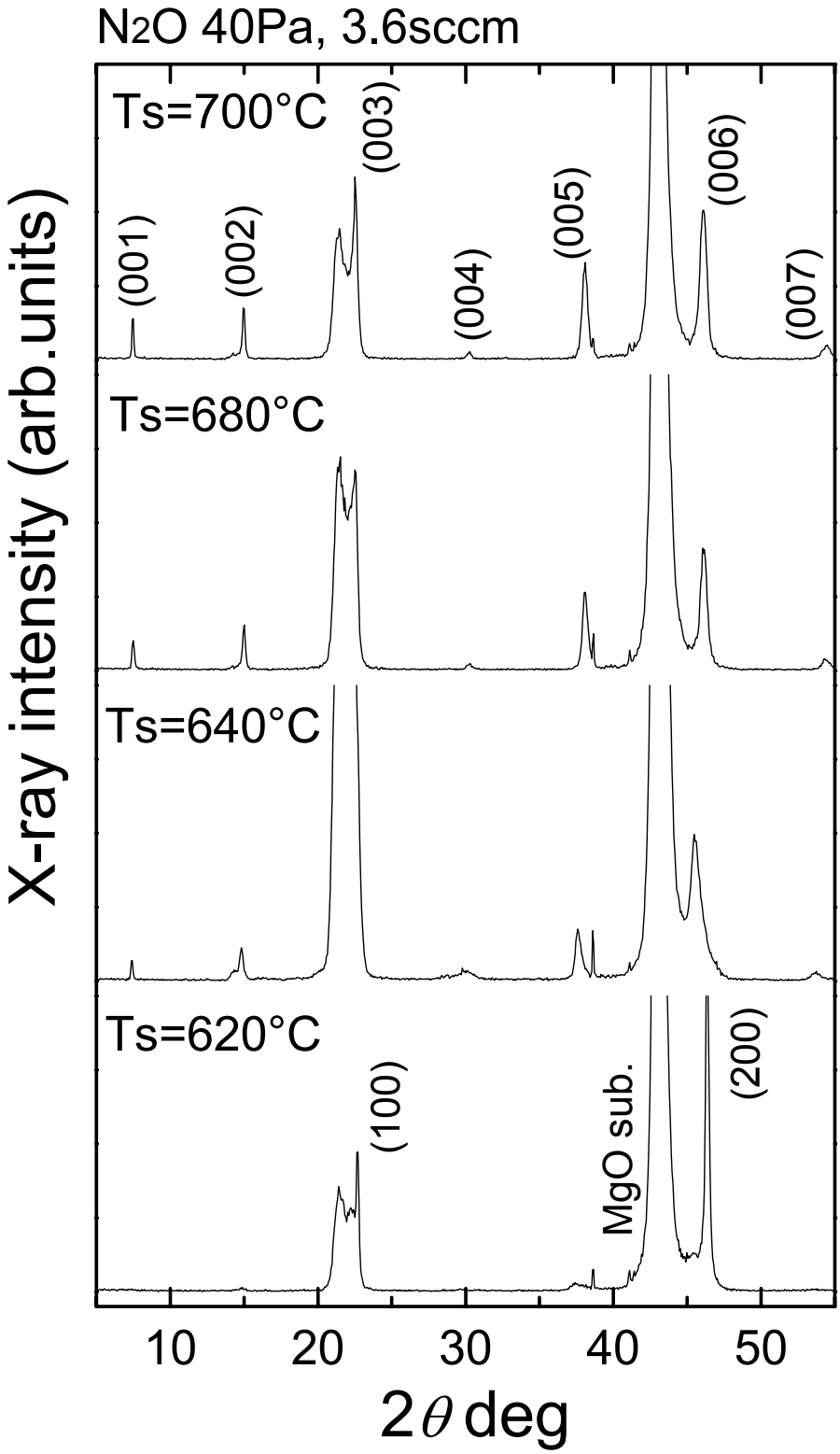


Fig.3 Substrate temperature dependence of XRD pattern for YBCO films.

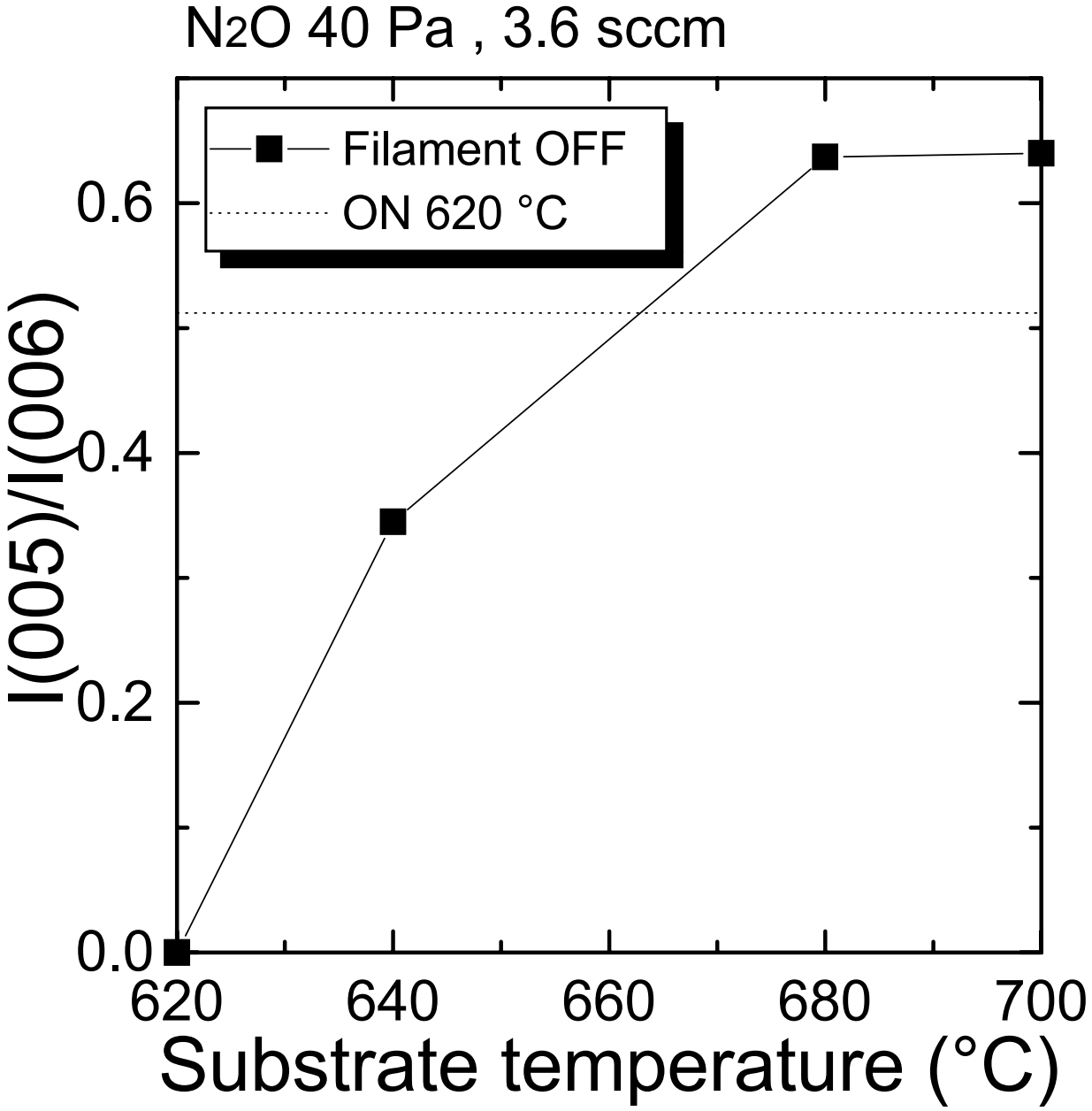


Fig.4. Intensity ratio of I(005)/I(006) of YBCO films as a function of the substrate temperature.

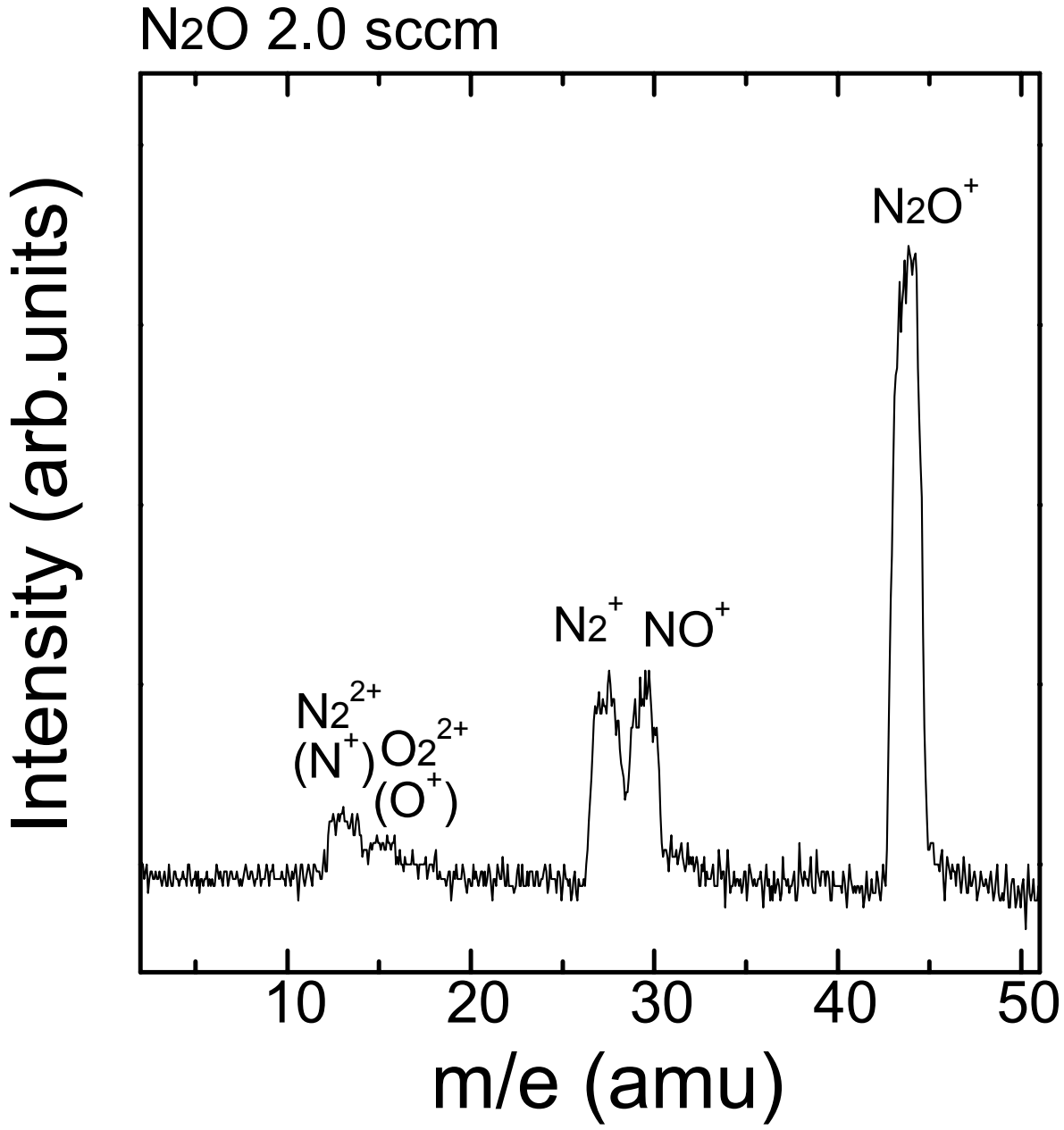


Fig 5. Mass spectrum of N_2O gas with the hot filament.

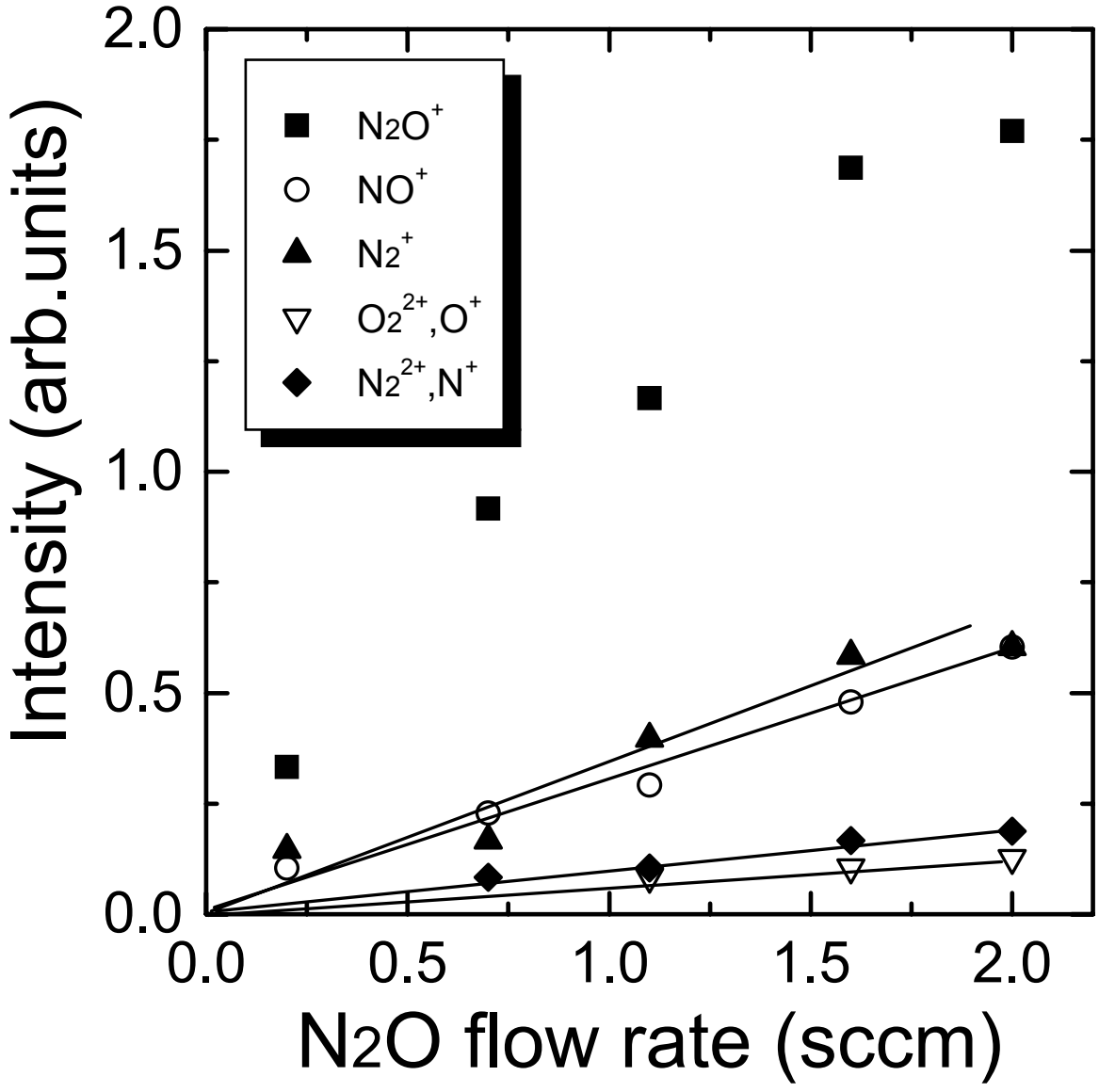


Fig 6. N_2O flow rate dependence of the respective mass peak intensities with the hot filament.

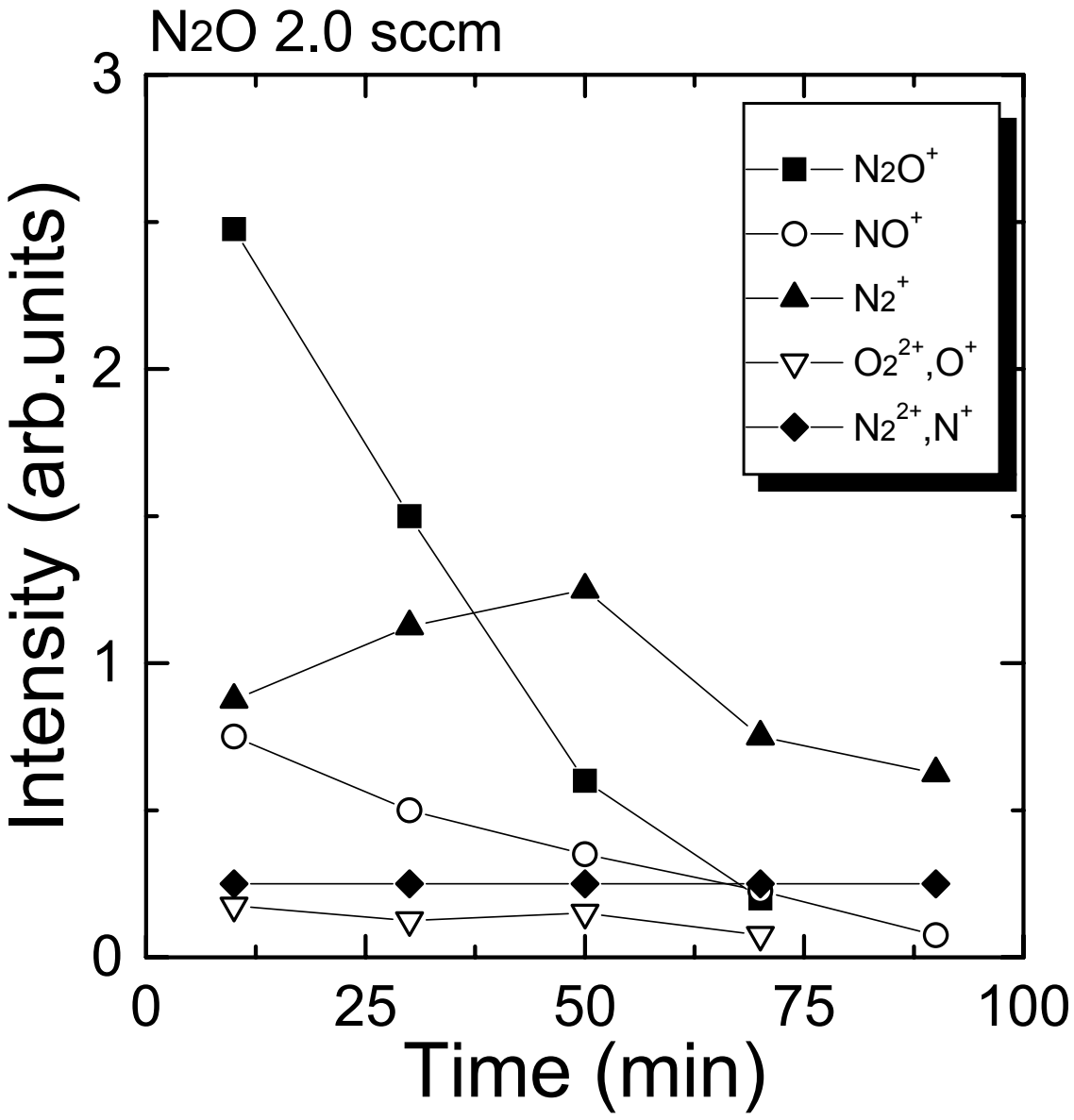
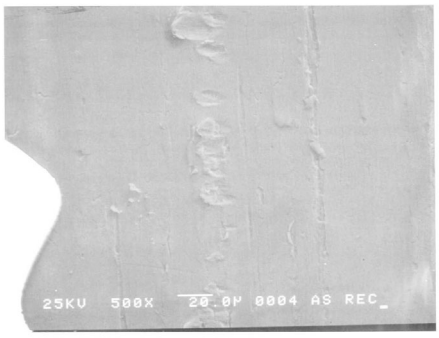
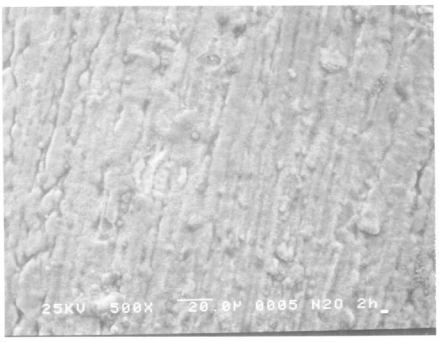


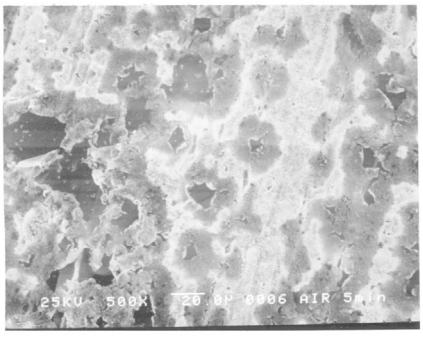
Fig.7 Time dependence of intensities of the respective mass peaks.



(a) before running of filament in N_2O



(b) after running of filament in air



(c) after running of filament in N_2O

Fig.8 SEM photographs of the filament surface before and after running of the filament.