Effect of nitrogen gas on preparation of Ti-Al-N thin films by pulsed laser ablation

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Abstract

The effect of ambient N_2 gas on the preparation of $Ti_{0.9}Al_{0.1}N$ (TAN) thin films for ferroelectric capacitors by pulsed laser ablation (PLA) using ArF and KrF excimer lasers was explored. The TAN films were prepared on (100)Si substrates heated at 620 ºC in various N_2 pressures ranging from vacuum to 130 Pa. The TAN crystal growth was found to be influenced by the content of unintentionally-incorporated O which was found to be controlled by the introduction of N_2 gas into the deposition chamber. The O content for films prepared by KrF was found to be smaller than that for films prepared by ArF because of the smaller optical absorption cross-section of KrF excimer laser for residual O_2 or H_2O molecules in the chamber and/or the higher deposition rate. The TAN film prepared by KrF excimer laser was found to be nearly epitaxial Si with a cube-on-cube crystallographic orientation.

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1. Introduction

$Pb(Zr,Ti)O_3$ (PZT) ferroelectric capacitors is a material employed to fabricate nonvolatile memory and requires oxidation-resistant electrodes. Pt is conventionally used as an electrode, but it creates fatigue when used with PZT[1], Pt hillocks form[2], the Pb loss is found to be from the PZT[3], and Pt reduces PbO in the presence of H_2 through a catalytic reaction[4]. TiN has been extensively studied for the diffusion barrier in advanced integrated-circuit devices, suggesting that TiN can be introduced without any difficulties into the present or future LSI process[5]. TiN, however, is not sufficiently oxidation-resistant[6] for the preparation of PZT. Thus, we proposed Ti-Al-N (TAN) as an oxidation-resistant electrode material for the PZT based on the idea that aluminum oxide is good barrier against oxidation[7]. Perovskite PZT film was found to be grown on the TAN electrode, resulting in a ferroelectric hysteresis loop. However, the interface layer of the TAN was oxidized to some extent by the PZT deposition due to a low quality of the TAN film[7]. In the present study, the effect of ambient N_2 gas on the preparation of TAN thin films by PLA is explored for high-quality film synthesis. Especially, from the viewpoint of the collision of depositing particles, including atoms, molecules, and clusters, with ambient gas molecules, the effect of ambient gas was examined.

2. Experimental

TAN films were deposited using ArF and the KrF excimer lasers (Shibuya ES5000) with wavelengths of 193 nm and 248 nm, respectively. The lasers were operated at a pulse repetition rate of 5 or 10 Hz. The fluence was 4.2 J/cm^2 for the ArF laser and 6.2 J/cm^2 for the KrF laser. Two

hot-pressed $Ti_{0.9}Al_{0.1}N$ targets were used; densities of 60 % (low density: LD) and 91 % (high density: HD) of ideal one. TAN films were prepared on (100)Si substrates heated at 620 ºC in various N_2 pressures ranging from vacuum to 130 Pa. Prior to film deposition, the chamber was evacuated to about 2×10^{-4} Pa using a diffusion pump. So, the present vacuum means the pressure of the residual gas of 2×10^{-4} Pa. The Si substrates were cleaned in a solution of HF, distilled water, and ethanol in the ratio of 1:1:10 to obtain a hydrogen-terminated Si surface. The KrF films are thicker than the ArF films by a factor of about two due to the difference in deposition rates.

3. Results and Discussion

3-1. TAN films prepared by ArF excimer laser with high and low density targets

Figure 1 shows the X-ray diffraction (XRD) patterns for films prepared on Si substrates by ArF excimer laser ablation at various N_2 pressures. Only the (200) diffraction peak of the TAN structure is observed for films prepared in vacuum and 1.3 Pa of N_2 gas. The peak is not observed when the N_2 pressure exceeds 13 Pa. This result suggests that highly [200]-oriented TAN films can be deposited in low N_2 pressure. Figure 2 shows the peak intensity of the (200) diffraction as a function of the N_2 pressure. In this figure, two sets of TAN films prepared using the LD and HD targets are compared. It was found that the crystal growth is enhanced by introducing N_2 gas into the deposition chamber while excess N_2 pressure suppresses the crystal growth. The XRD rocking curve measurement on the (200) diffraction revealed that the full width at half maximum (FWHM) for the films prepared with the HD target is decreased from 4.5 ° to 3.1° by increasing the N_2 pressure from vacuum to 1.3 Pa.

Fig. 2 also suggests that the HD target enhances the crystal growth, when compared with

films formed from the LD target. The FWHM of the XRD rocking curve for the films prepared using the HD target was also smaller than that for the films prepared with the LD target. The use of the HD target in PLA may reduce the thickness of the molten layer as a consequence of more intense laser absorption in the HD target than in the LD target. This increases the temperatures of the molten layer of the target surface and the temperature of the ejected clusters, and/or increases the kinetic energy of depositing particles due to the PLA explosion[8].

The film composition was evaluated by electron-probe microanalysis (EPMA). The ratio of Al to Al + Ti was found to be approximately10 % and nearly the same as the ratio in the target. Figure 3 shows the O content as a function of the N_2 pressure. It was found that the O content of the deposited films is large and ranges from 30 to 40 % for the films prepared using the HD target although the evaluation of the TiN composition by EPMA includes some ambiguity because of the overlapping of the N K_α and Ti L_l lines[9]. The presence of a large amount of O was also confirmed by X-ray photoelectron spectroscopy (XPS). Despite the large O content, XRD spectra revealed a TAN crystal with a single phase. The EPMA measurement revealed that the O content decreased with increasing N_2 gas to 1.3 Pa, and then increased by further pressure increase to 130 Pa. This minimum in Fig.3 is well correlated with the (200) peak intensity as a function of the N_2 pressure. In other words, the TAN crystal growth seems to be governed by the O impurity content.

The dependence of the (200) diffraction intensity on the N_2 pressure might be explained as follows. In ultrahigh vacuum TAN particles ejected from the target might be expected to evolve some N atoms during the flight process, resulting in a N-deficient film. For instance, AlN is thermally decomposed above 2400 ºC into Al metal and N_2 gas[10]. In the present vacuum, there exist residual gases consisting of H_2O and O_2 gases with a background pressure of 2×10^{-4} Pa. There is a possibility that the TAN particles with N deficiency react with the ambient oxidation gas

during the flight process, resulting in the oxi-nitride. In this deposition condition, if N_2 gas with a pressure far larger than the residual oxidation gas is present, ejected TAN particles collide with N_2 rather than O_2 with a higher probability, thus reducing the N deficiency and the O impurity. Excess amount of the ambient N_2 causes cooling or deactivation of the depositing particles due to excess collisions with N_2. Besides, the excess N_2 also causes the oxidation of depositing particles due to the excess collisions with N_2 and oxidation gases. These mechanisms probably lead to the serious degradation of the TAN crystal.

Only for the TAN-resistivity measurement, (100)MgO substrates are used because of the rather low resistivity of the Si substrate. Resistivity of the TAN films increases with an increase in the N_2 pressure up to 130 Pa, from 160 μΩ·cm to 10 mΩ·cm. Minimum resistivity of 160 μΩ·cm was obtained in vacuum, and the resistivity was increased to be about 200 μΩ·cm by N_2 gas up to 1.3 Pa .

Figure 4 shows the photographs of the scanning electron microscopy (SEM) for the films prepared in various N_2 pressures. The formation of droplets was found to be largely increased by the N_2 pressure of 130 Pa while there was no appreciable change up to 13 Pa. This suggests that the film deposition was governed by the cluster deposition rather than the atomic or molecular deposition. In vacuum or low N_2 pressure, clusters, including droplets, ejected from the target coalesce into the film because they are still sufficiently "hot". However, they may not coalesce into the film under the high pressure condition because of the increased collisional cooling of depositing clusters. This may explain the remaining of droplets on the film surface as the N_2 pressure is increased.

3-2. TAN films prepared by KrF excimer laser with the HD target

Figure 5 shows the XRD intensity of the (200) diffraction of TAN normalized by the film thickness as a function of N_2 pressure for the KrF films. For comparison, data for ArF films are also shown. Comparison of the (200) intensity for the films with a laser repetition rate of 10 Hz and at N_2 pressure of 1 Pa shows that the crystal growth is enhanced by using KrF excimer laser instead of ArF excimer laser. Furthermore, the O content in the KrF films grown at 5 and 10 Hz was found to be reduced to be about 20 %, which is smaller than that in the ArF films grown under the similar condition. The low oxygen content in the KrF film might be explained in terms of the low optical absorption cross-section of KrF excimer laser for the residual H_2O or O_2 molecules, and/or the high deposition rate.

From Fig. 5 the reduction of the repetition rate was found to suppress the crystal growth, contrary to what is observed in other deposition schemes. It is known that the crystal growth is enhanced by lowering the deposition rate. This opposite behavior might be explained by the cluster-deposition which was discussed earlier. In this model, the surface crystal- growth is enhanced by the high temperature of the molten layer on the substrate due to the subsequent deposition of hot clusters. Figure 6 shows X-ray pole figure for the KrF film using the TAN (202) plane. This figure revealed that the normal direction of this plane is directed to $\Psi = 45$ °, and this plane has four-fold rotational symmetry without any trace of other orientations although some fluctuation can be seen along the direction of Φ. This result suggests that the TAN film is nearly epitaxially grown on Si substrate having cube-on-cube crystallographic orientation.

4. Conclusions

The TAN crystal growth was found be influenced by the content of O unintentionally-incorporated which can be controlled by the introduction of N_2 gas. The O content

for the KrF film was found to be smaller than that for the ArF films because of the smaller optical absorption cross-section of KrF excimer laser for residual O_2 or H_2O molecules and/or the higher deposition rate. The KrF film was found to be nearly epitaxially grown on Si substrate with cube-on-cube crystallographic orientation.

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FIGURE CAPTIONS

Fig. 1. XRD patterns for TAN films prepared on (100)Si substrates using the HD target by ArF excimer laser at various N_2 pressures. Small peak around 33 deg is the diffraction from Si (200) plane.

Fig. 2. Peak intensity of the (200) diffraction as a function of the N_2 pressure for films prepared on Si substrates by ArF excimer laser. LD and HD represent the low density and the high density targets, respectively.

Fig. 3. O content as a function of the N_2 pressure for TAN films prepared on Si substrates using the low and high density targets by ArF excimer laser.

Fig. 4. SEM photographs for films prepared on Si substrates using the high density target by ArF excimer laser in various N_2 pressures.

Fig. 5. XRD intensity of the TAN (200) diffraction normalized by the film thickness as a function of N_2 pressure for the films prepared by KrF excimer laser. For comparison, data for ArF excimer laser are also shown.

Fig. 6. X-ray pole figure for the film prepared on the Si substrate using the high density target by KrF excimer laser using the TAN (220) plane.

Total: 2,300 words + 200 words x 6 figures = 3,500 words ; limits: 3,500 words / 6 printed pages

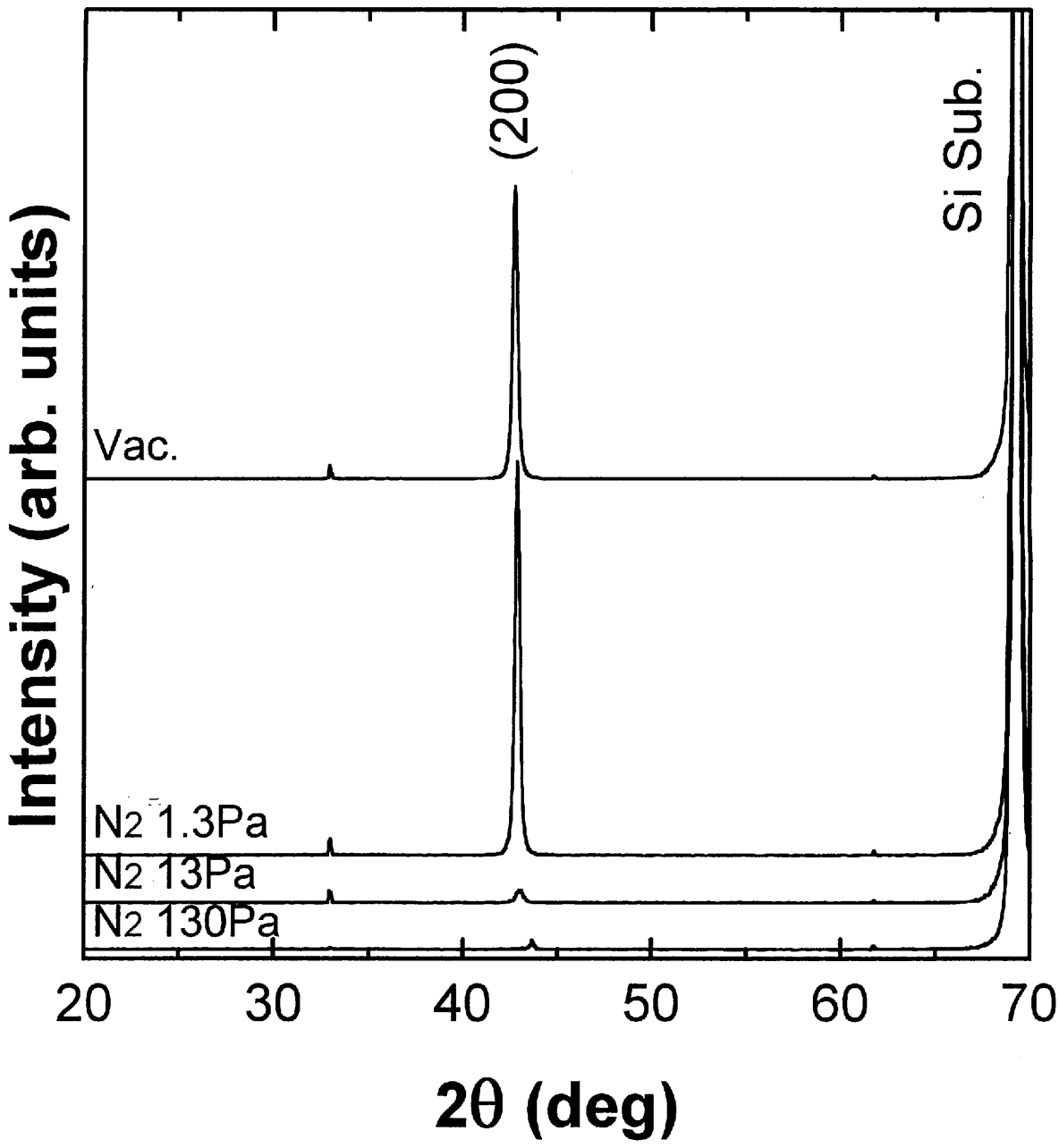


Fig.1 A. Morimoto

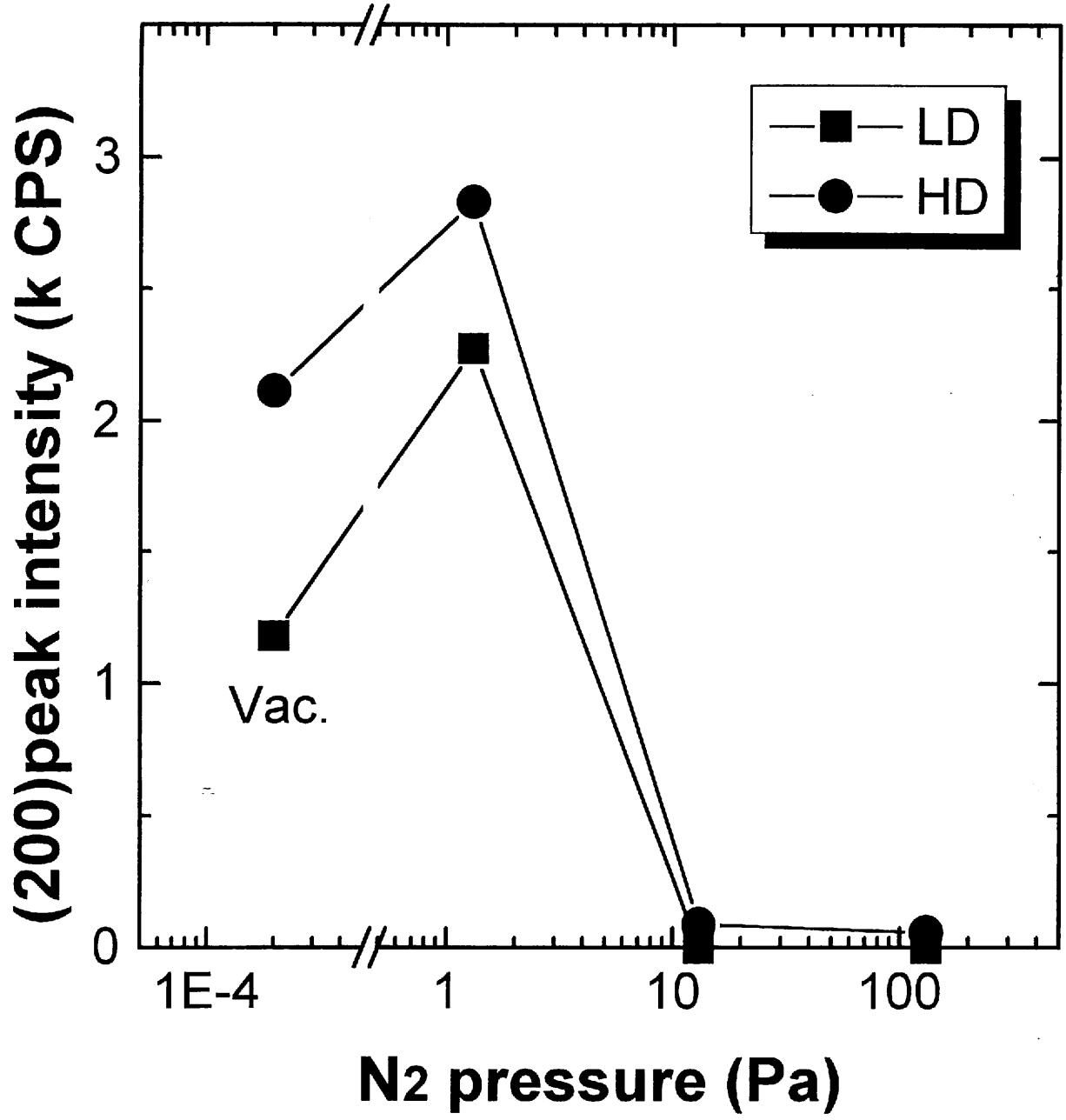


Fig. 2 A. Morimoto

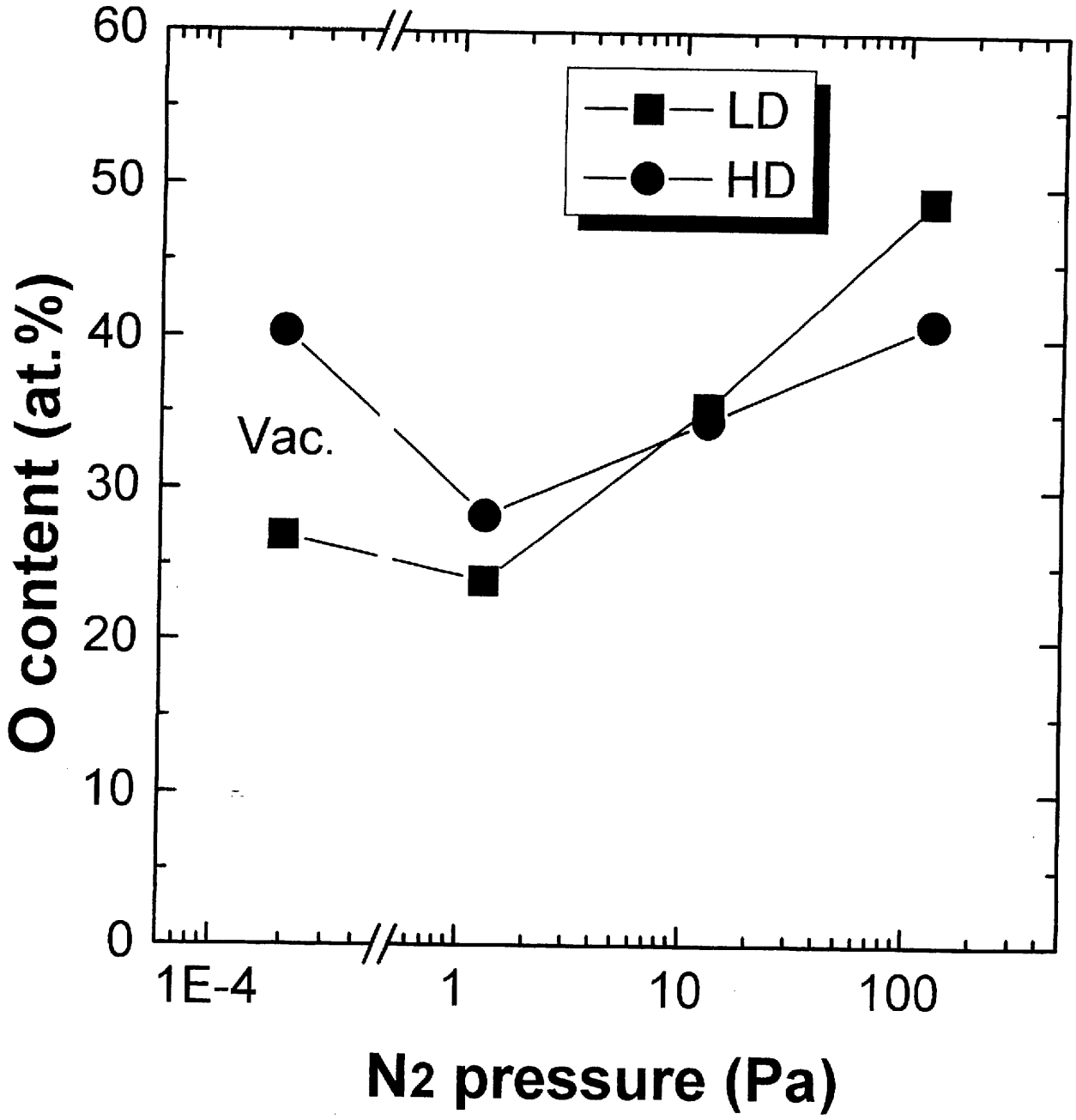
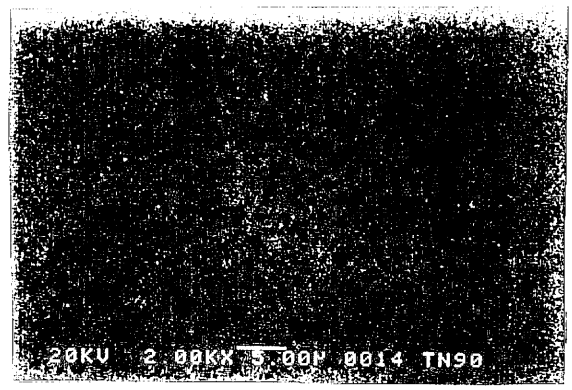
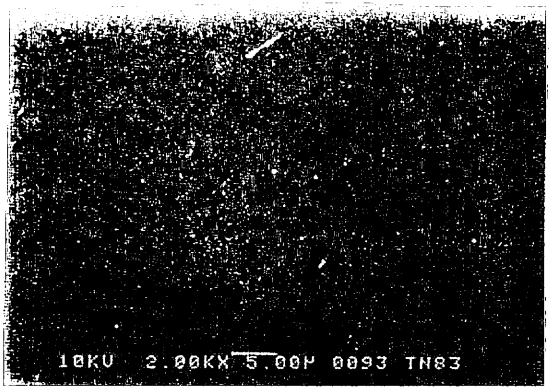


Fig. 3 A Morimoto

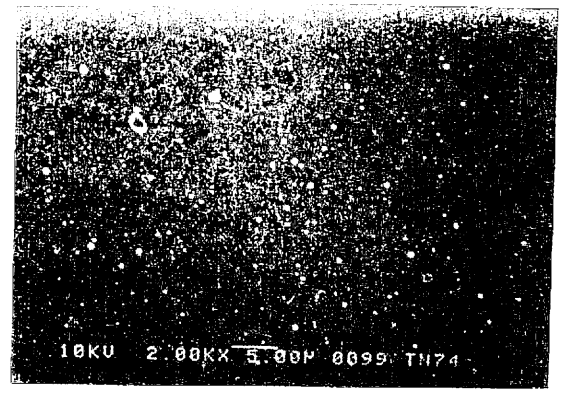
a) Vac.



b) 1.3Pa



c) 13Pa



d) 130Pa

Fig.4 A. Morimoto

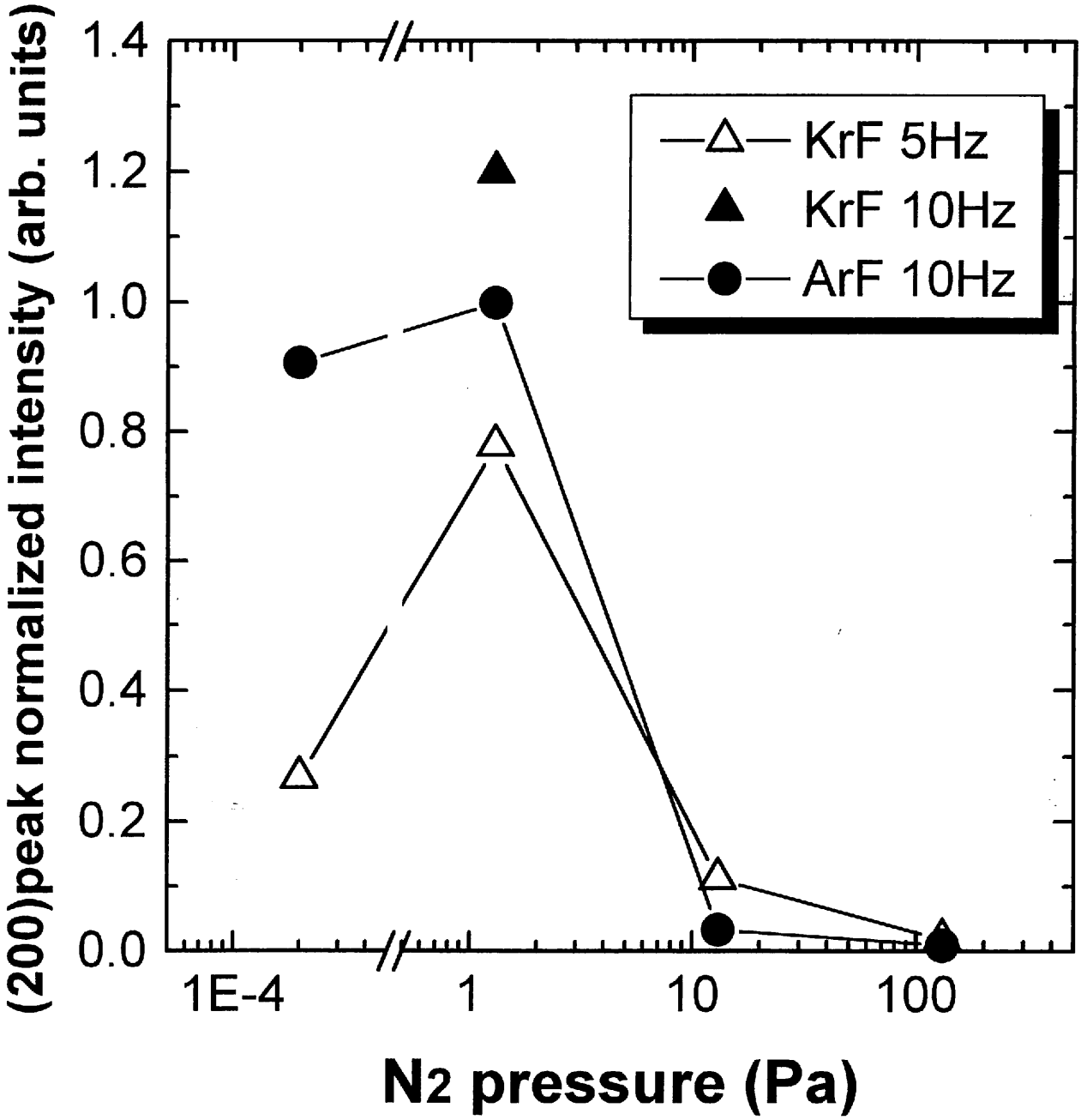


Fig 5 A. Morimoto