Dissociative adsorption and subsequent reactions of methane on Ar-ion sputtered single crystal of LiNbO$_3$

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Abstract

The states of adsorption of methane on an Ar-ion sputtered single crystal of LiNbO$_3$ have been studied with X-ray photoelectron spectroscopy (XPS). Methane reacted with the oxygen species of O$^-$ ion to oxidized products such as carbonyl and/or carboxyl products at room temperature. The degree of subsequent reaction from a methoxide to a carboxyl group depends on not only the exposed pressure of methane, but also the time of sputtering. Longer sputtering increased the quality of highly reactive oxygen species O$^-$ on a surface of LiNbO$_3$, and progressed the degree of oxidized states of products by subsequent reaction with the other O$^-$ species. The levels of frequency of impingement of the reactant gas to the surface of a sputtered sample are important to control a degree of stage of the oxidation of methane. A higher pressure makes it easy to progress to a subsequent reaction by raising the frequency of impingement of the reactant gas to the surface of a sample. © 1998 Elsevier Science B.V.

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1. Introduction

The chemistry of methane is presently of great importance. Industrially, the desire to make more efficient commercial use of natural gas, of which methane is the major constituent, has been increased. Oxidative coupling, steam reforming, and direct selective oxidation to methanol, and so on have been widely examined.
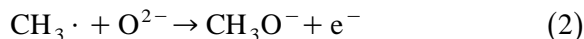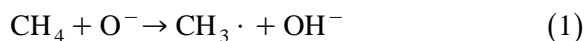
The primary step in methane activation is generally considered to be the rupture of the C–H bond [1]. Experimental evidence of Lee et al. [2,3] obtained via molecular beam techniques has established that the dissociation of methane on the Ni(111) surface led to surface methyl species and hydrogen atoms. The methyl species was reported to undergo dehydrogenation and oligomerization as the surface temperature was increased to form CH$_2$, CH, C, C$_2$H$_2$ and C$_6$H$_6$ species, as identified by high resolution electron energy loss spectroscopy (HREELS).

There have been very few studies of interaction of methane with oxides, and all of them deal with the reaction of CH$_4$ with surface monooxygen anion radical O$^-$. Kaliaguine et al. studied the interaction of CH$_4$ with O$^-$ formed by γ-irradiation of V$_2$O$_5$/SiO$_2$ [4]. The EPR signal of O$^-$ was destroyed on admission of CH$_4$. The reaction of methane with O$^-$, both in

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the presence and absence of oxygen in the gas phase, yielded similar products. This was explained by the formation of stable surface alkoxide species according to the following reactions:

$$CH_4 + O^- \rightarrow CH_3 \cdot + OH^- \qquad (1)$$

$$CH_3 \cdot + O^{2-} \rightarrow CH_3O^- + e^- \qquad (2)$$

or

$$CH_3 \cdot + O^- \rightarrow CH_3O^- \qquad (3)$$

Liu et al. found CH_4 to interact with O^- which was produced by the decomposition of nitrous oxide on MoO_3/Cab-o-Sil at $-196°C$ to produce $CH_3.$ and at $25°C$ to give CH_3O^- [5]. Ito et al. studied the oxidative dimerization of methane over a lithium promoted magnesium oxide catalyst at $650°C$ [6]. They reported that $[Li^+O^-]$ centers probably were the active sites responsible for initiating the reaction by abstracting a hydrogen atom from CH_4.

$$Li^+O^- + CH_4 \rightarrow Li^+OH^- + CH_3 \cdot \qquad (4)$$

Mehandru et al. studied the role of O^- surface radicals for methane C–H bond activation on MoO_3 with molecular orbital theory [7]. They concluded that the resulting activation energy was calculated to be 0.7 eV. This barrier is low, whether the O^- was created by UV (O $2p \rightarrow Mo\ 4d$) charge-transfer excitation or whether they are present due to the nonstoichiometry resulting from cation vacancies.

$$Mo^vO^- + CH_4 \rightarrow Mo^vOH^- + CH_3 \cdot \qquad (5)$$

They also studied the subsequent reactions of methyl radicals on MoO_3 [7]. They reported that the methyl radical would be mobile over the O^{2-} basal plane sites of MoO_3, but when it came to another O^-, it would bind as methoxy, being trapped approx. 2.5 eV as the electron–hole pair recombination energy. In the presence of adjacent O^-, activated hydrogen loss from methoxy is possible, resulting in the formation of formaldehyde, OH^-, and Mo^v. Additional O^- sites should activate the C–H bonds in formaldehyde to yield more highly oxidized

products. They expressed finally that the variations in products with MoO_3 suggested there was much to learn about influences from the surface structure of a sample.

In this report, we studied the surface states of Ar-ion sputtered $LiNbO_3$, and their effects on methane C–H bond activation and subsequent reactions. The presence of oxygen vacancies, Nb^{4+} and O^- ions after irradiation treatment have been reported with optical absorption and ESR [8,9]. It is worthwhile to clarify the role of O^- and of a defective surface for methane activation and subsequent reactions on Ar-ion sputtered single crystals of $LiNbO_3$ for designing a direct selective oxidation catalyst.

2. Experimental

A single crystal of $LiNbO_3$ was obtained from Nippon Kessho Kogaku. The size of sample was 13 mm $\times$ 13 mm square, and the thickness was 1 mm. This plate was polished to optical finish by the manufacturer. The sample plate was z-cut (z axis normal to a plane).

X-ray photoelectron spectroscopy (XPS) experiments were performed with an angle resolved Shimadzu ESCA-KM spectrometer, which was equipped with a concentric hemispherical analyzer. A MgKα (1253.6 eV) X-ray source was used for the excitation. The spectrometer was operating under a base pressure of 7×10^{-8} Pa in the chamber. The exposure of methane was carried out in the preparation chamber of XPS. The binding energy (BE) was calibrated with the Nb^{5+} ($3d_{5/2}$) peak at 207.0 eV. Photoelectron spectroscopies were detected at an angle of 15° to the surface of a sample. The treatment of the acquired spectrum was carried out with the software 'Vision' produced by Kratos Analytical. The atomic ratio of each element was calculated from each peak intensity with the sensitivity factor by Wagner [10].

CH_4 gas (UHP grade: $> 99.99995\%$) was obtained from Ueno Gas. The exposure of
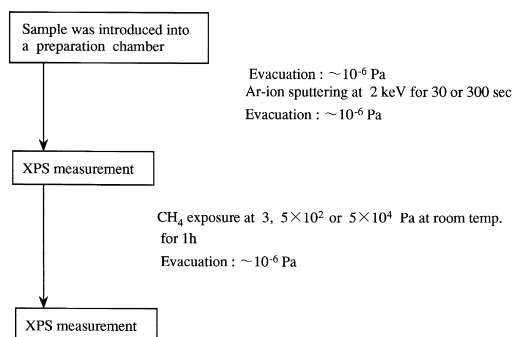
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┌─────────────────────────────┐
│ Sample was introduced into  │
│ a preparation chamber       │
└─────────────────────────────┘
              │        Evacuation : ∼10⁻⁶ Pa
              │        Ar-ion sputtering at 2 keV for 30 or 300 sec
              │        Evacuation : ∼10⁻⁶ Pa
              ▼
┌─────────────────────────────┐
│ XPS measurement             │
└─────────────────────────────┘
              │        CH₄ exposure at 3, 5×10² or 5×10⁴ Pa at room temp.
              │        for 1h
              │        Evacuation : ∼10⁻⁶ Pa
              ▼
┌─────────────────────────────┐
│ XPS measurement             │
└─────────────────────────────┘
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Fig. 1. XPS experimental procedure.

methane was performed according to the procedure shown in Fig. 1.

3. Results

A sample of $LiNbO_3$ was pretreated by Ar-ion sputtering, and then was exposed to methane at room temperature as shown in Fig. 1. The spectrum for C 1s has no clear peak without methane exposure after Ar-ion sputtering at 2 k eV for 30 s as shown in Fig. 2(A). The spectrum (B) is the result for exposed sample under the pressure of methane at 5×10^4 Pa after Ar-ion sputtering for 30 s. This spectrum has two peaks. One peak noted as (a) has a peak position at 285.0 eV. The peak position of an alkane such as methane is known at 285.0 eV [11]. Vohs and Barteau studied adsorbed intermediates in the reactions of acetone and 2-propanol on the ZnO [12]. They reported that the peak of a pendant methyl group in intermediates on ZnO appeared at 285.2 eV, and a π-bonded moiety such as π-propargyl species gave a characteristic peak at 285.0 eV. We suspect this peak comes from a molecularly adsorbed methane on the defective surface of $LiNbO_3$ at room temperature. The second peak noted as (b) has the peak position at 289.6 eV. Barteau et al. reported that the binding energies of formate species on ZnO and MgO were 289.2 eV [13] and 290.3 eV [14], respectively, and a molecularly formaldehyde exhibited at 289.4 eV [14]. Roberts and Smart

studied CO adsorption on NiO, and assigned the carbonaceous product at 290.8 eV on the C 1s spectrum to surface carbonate [15]. The spectrum (C) shows the result of the exposed sample under the same pressure, however, the time of pretreatment by Ar-ion sputtering is 300 s. This spectrum also has two clear peaks. The peak positions of these two peaks were the same with those for the spectrum (B). However, the photo-line of peak (a) on the spectrum (C) seems to become broader than that on the spectrum (B). We deconvoluted the peak (a) to two peaks, and these peaks were autofitted with the software 'Vision' produced by Kratos Analytical. The obtained values of the two peaks were 285.0 and 286.5 eV. The peak (a) on the spectrum (B) was deconvoluted to the same position as shown in Fig. 2. Barteau et al. reported that the peak of methoxy species on ZnO and TiO_2 appeared at 286.8 eV, and methoxide on MgO appeared at 287.4 eV [13,14,16]. The other small peak can be seen in Fig. 2(C) near 281.0 eV. Since C 1s binding energies for adsorbed alkyl groups are typically less than 284 eV [17,18], and the peak at 283.7 eV was assigned to the adsorbed methyl group on ZnO [12], the small peak near 281.0 eV should be a more carbonized species. From these spectra (B) and (C) for C 1s, methane
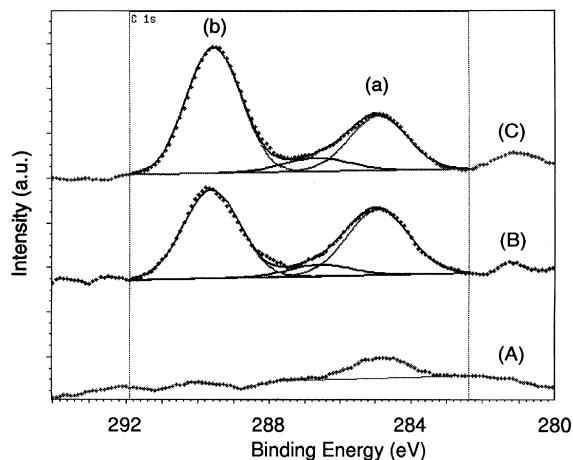

Fig. 2. C 1s XP-spectra of Ar-ion sputtered $LiNbO_3$. (A) After the sputtering for 30 s. (B) and (C) The sample was exposed to methane at room temperature under the pressure of 5×10^4 Pa for 1 h after the sputtering for 30 s (B) and 300 s (C).
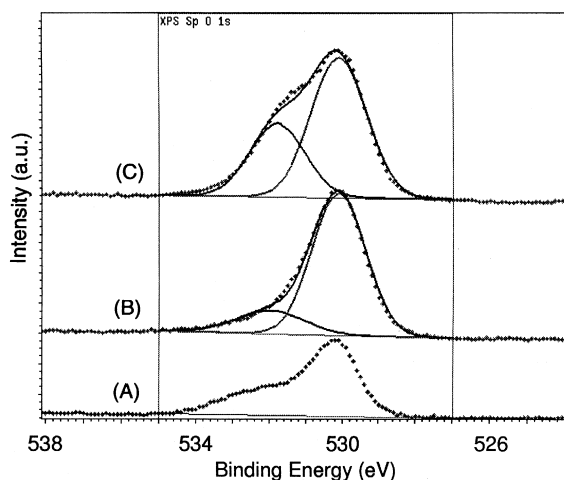
Fig. 3. O 1s XP-spectra of a single crystal of $LiNbO_3$. (A) The sample as supplied. (B) After the sputtering for 300 s. (C) The sample was exposed to methane at room temperature under the pressure at 5×10^4 Pa for 1 h after the sputtering for 300 s.

adsorbed on the defective surface of $LiNbO_3$, and this molecularly adsorbed methane reacted to carboxyl or carbonyl species at room temperature. The intensity ratio of peak (b) to (a) was increased with the increase of sputtering time. This means that the reaction with oxygen is enhanced by longer sputtering time.

Fig. 3 shows the spectra for the O 1s level of the pretreated sample which was sputtered for 300 s shown as (B) and for the exposed one under the pressure of methane at 5×10^4 Pa for 1 h after the sputtering shown as (C). Fig. 3(A) shows the O 1s spectrum for the sample as supplied. The peak position of spectrum (B) was 530.1 eV. This peak can be assigned to the O^{2-} species associated with the $LiNbO_3$ lattice.

The spectrum (B) is asymmetric, even though the sample was sputtered for 300 s, and is able to be deconvoluted to two peaks by the software as shown in Fig. 3(B). The deconvoluted spectra were autofitted. The peak position of another deconvoluted peak was 531.9 eV, and this peak can be assigned to the O^- species which has been reported on the irradiated surface of $LiNbO_3$ by Ar-ion bombardments [19,20]. The atomic ratios of these O^{2-} and O^- to niobium are listed with that of lithium on a Table 1. The shoulder peak of O1s was enlarged clearly after the exposure as shown in Fig. 3(C). The discernment of the photoline of O 1s for oxidized products, which were considered in Fig. 2(B) and (C), seems to be impossible. Because each oxidized product is not clear, and a hydroxyl ion (531.0 eV) should be included in this shoulder peak of the O 1s spectrum [21]. However, the enlargement of this shoulder is ascribed to the production of the oxidized species as shown in Fig. 2(B) and (C).

The spectrum of the untreated sample shows doublet peaks of $Nb3d_{5/2}$ and $Nb3d_{3/2}$ as shown in Fig. 4(A), and these peak positions agreed with the reported values (207.0 and 209.8 eV) [19]. The spectrum (B) in Fig. 4 shows that of the Ar-ion sputtered sample. The time for sputtering is 300 s. The spectrum (B) shows the presence of lower valence of the niobium ion (Nb^{4+} and Nb^{3+}) [19,20]. The percentage of lower valence of the niobium ion to total niobium ion is listed in Table 1. 77% of the niobium ions was reduced by this Ar-ion sputtering, and this value changed with sputtering

Table 1
The ratios of Li/Nb, O/Nb and lower valence niobium ion to total niobium ion based on XPS intensities

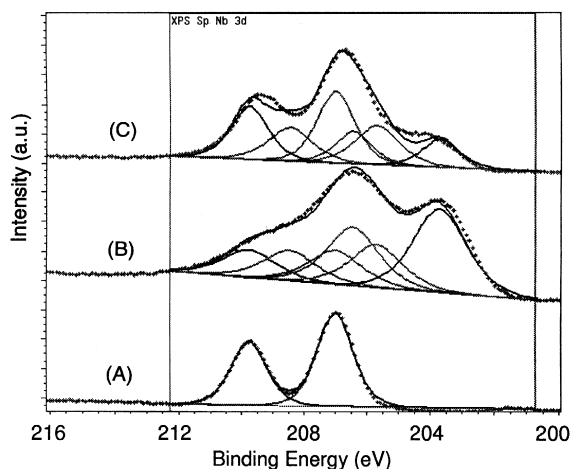| Sputtering time (s)	The atomic ratios after Ar-ion sputtering			CH_4 exposure under 5×10^4 Pa for 1 h after the sputtering	
	Li/Nb	O/Nb	$Nb^{4+} + Nb^{3+}$/Nb	Li/Nb	O/Nb
0	0.49	2.65	0		
30	0.12	2.21	0.60	0.88	3.26
		(O^{2-}/Nb 1.99, O^-/Nb 0.22)			
300	0.02	1.75	0.77	0.35	3.18
		(O^{2-}/Nb 1.37, O^-/Nb 0.38)			

Fig. 4. Nb 3d XP-spectra of a single crystal of LiNbO₃. (A) The sample as supplied. (B) After Ar-ion sputtering for 300 s. (C) The sample was exposed to methane at room temperature under the pressure at 5×10^4 Pa for 1 h after the sputtering for 300 s.

time. The reduced niobium ion was partly oxidized again by the exposure of methane at room temperature as shown in Fig. 4(C). We tried to clarify the reason why the reduced niobium ion was oxidized again by the exposure of methane.

The surface atomic ratios of Li/Nb and O/Nb after the exposure are listed on the right side of Table 1. Since both of these values increased after the exposure, we considered that the migration of subsurface ions for lithium and oxygen to the top of the surface occurred after the exposure at room temperature. We also measured the change of these surface atomic ratios at a detected angle of 90° to the surface of the sample. The result is shown in Table 2 with that of 15°. The depth of observed information at an angle of 90° is almost five times deeper than that of 15°. The surface atomic ratio of oxygen is the same, and that of lithium is just a

little bit larger at 90° after the Ar-ion sputtering. Both of these ratios of lithium and oxygen increased after the exposure. Since these ratios for the sample before the exposure are smaller than those for that after the exposure, we consider lithium and oxygen ions migrated from the subsurface to the surface. This migrated oxygen, particularly O^- ion seems to partly oxidize the lower valence niobium ion as shown in Fig. 4(C) because this oxygen species is the most reactive oxygen species [22]. This O^- species abstracts a hydrogen atom from methane, and reacts subsequently with another O^- ion to produce more oxidized products on the surface. Since these reactions occur mainly on the surface, the value of O/Nb for the exposed sample at an angle of 15° has the largest one.

The dependency of the degree of oxidization for methane on the pressure of exposure was examined. Fig. 5(A), (B) and (C) show each a spectrum for C 1s of the exposed sample under a pressure of 3, 5×10^2 and 5×10^4 Pa, respectively. The duration time for Ar-ion sputtering and the exposure time for methane are the same for this sample. Fig. 5(C) is the same as Fig. 2(B), but the scale of every spectrum is adjusted for convenience to compare. The spectrum (A) was deconvoluted, and autofitted to three peaks (285.0, 286.5 and 288.8 eV). The surface atomic ratios of these deconvoluted peaks to niobium were 1.01, 0.25 and 0.20 in order of binding energy. Methane adsorbed easily at room temperature on the defective surface under comparative low pressure as shown in Fig. 5(A). Under this pressure, some of the adsorbed methane reacts with O^- to methoxide or methanol at room temperature as shown by the deconvoluted

Table 2
The ratio of Li/Nb and O/Nb based on XPS intensities

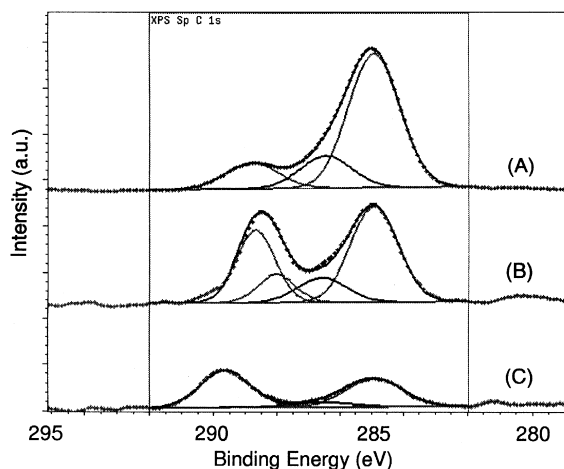| Detected angle	The atomic ratios of a sample after the sputtering for 300 s		CH₄ exposure under 5×10^4 Pa for 1 h after the sputtering for 300 s	
	Li/Nb	O/Nb	Li/Nb	O/Nb
15°	0.02	1.75	0.35	3.18
90°	0.11	1.76	0.23	2.43

Fig. 5. C 1s XP-spectra of Ar-ion sputtered $LiNbO_3$. The sample was exposed to methane at room temperature under the pressure at 3 Pa (A), 5×10^2 Pa (B) and 5×10^4 Pa (C) for 1 h after the sputtering for 30 s.

photolines at 286.5 and 288.8 eV in Fig. 5(A). The ratio (C/Nb) of the deconvoluted spectrum at 285.0 eV decreased from 1.01 to 0.64, but that of the spectrum at 288.8 eV increased from 0.2 to 0.61 under the exposure at 5×10^2 Pa. In Fig. 5(B), the fourth deconvoluted peak was needed to be fully autofitted. The peak position of this spectrum was 288.0 eV, and this value is close to that of a molecularly adsorbed methanol [13,14,16]. The ratio of the peak at 285.0 eV decreased more to 0.21, and the peak of the deconvoluted photoline 288.8 eV shifted to 289.7 eV under the 5×10^4 Pa exposure. This position of the peak was assigned to carbonyl or carboxyl species. The ratio of this deconvoluted photoline to niobium was 0.24. The ratio of molecularly adsorbed methane under a pressure of 5×10^4 Pa is clearly smaller than that under a pressure of 5×10^2 Pa, and the oxidization progressed as shown on the shift of the peak position from 288.8 to 289.6 eV.

4. Discussion

The single crystal of $LiNbO_3$ without being pretreated by Ar-ion sputtering did not react with methane at all even at 400°C, and any

traces of oxidized products were not observed on the XPS spectrum. The high reactivity of oxygen species of O^- was confirmed by the production of oxidized species from methane at room temperature as shown in Figs. 3 and 5. Since abstraction of hydrogen atoms from methane and the addition of oxygen on methyl radicals are possible at room temperature, the O^- species on the Ar-ion sputtered surface can overcome the barrier needed for the rupture of the C–H bond of methane. A molecular orbital study on the reaction of methane with the O^- hole center on the surface of MoO_3 was carried out by Mehandru et al. and they reported that the C–H bond activation barrier was calculated to be 0.7 eV [7]. This prediction of a low C–H bond scission barrier seems to be adoptable to explain a high activation at room temperature on Ar-ion sputtered surfaces of $LiNbO_3$, which has the O^- species.

The degree of subsequent reaction is clearly different in the exposed pressure of methane as shown in Fig. 5. The degree of oxidation from methane progressed with the increase of pressure. The pressure makes it easy to progress to a subsequent reaction by raising the frequency of impingement of the reactant gas to the surface of a sample.

The differences of time for Ar-ion sputtering also bring that of a degree of subsequent reactions as shown in Fig. 2. Table 3 is the result of a surface atomic ratio of each deconvoluted photoline of carbon species to niobium atom. The subsequent reaction to higher oxidized products progressed after longer Ar-ion sputtering. We considered how much did change on several factors which might affect a degree of

Table 3
The deconvoluted ratios of C/Nb based on the XPS photolines after CH_4 exposure under 5×10^4 Pa for 1 h

Sputtering time (s)	C1/Nb (285.0 eV)	C2/Nb (286.5 eV)	C3/Nb (289.6 eV)
30	0.20	0.01	0.26
300	0.16	0.06	0.37

subsequent reactions during Ar-ion sputtering from 30 till 300 s as shown in Table 1. All factors, namely, the oxygen vacancies, lower valence of niobium ions, oxygen species of O^- and loss of lithium, increased during the elongation of the sputtering time from 30 to 300 s. The increase of oxygen vacancies and loss of lithium seems to assist a subsequent reaction to higher oxidized products. Because oxygen vacancies of O^{2-} and loss of lithium on the surface seem to accompany the oxygen species of O^-, and this highly reactive oxygen species reacted with methane at room temperature.

5. Conclusions

The oxygen species of the O^- ion was observed on an Ar-ion sputtered surface of single crystal of $LiNbO_3$ with XPS. This species of the O^- ion abstracted hydrogen atoms from methane and reacted subsequently to oxidized products at room temperature. The degree of subsequent reaction from a methoxide to a carbonate depended not only on the exposed pressure of methane, but also on the sputtering time. We concluded as follows.

(1) Longer sputtering increased the quantity of highly reactive oxygen species O^- on a surface of $LiNbO_3$, and progressed the degree of oxidized states of products by subsequent reaction with the other O^- species.

(2) The levels of frequency of impingement of the reactant gas to the surface of a sputtered sample are important to control a degree of stage of the oxidation of methane. Higher pressure make it easy to progress to a subsequent reaction by raising the frequency of impingement of the reactant gas to the surface of a sample.

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