Plasma-Assisted Chemical Vapor Deposition of Titanium Oxide Films by Dielectric Barrier Discharge in $TiCl_4/O_2/N_2$ Gas Mixtures

Plasma-Assisted Chemical Vapor Deposition of Titanium Oxide Films by Dielectric Barrier Discharge in $TiCl_4/O_2/N_2$ Gas Mixtures[*]

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Abstract Low-pressure dielectric barrier discharge (DBD) $TiCl_4/O_2$ and N_2 plasmas have been used to deposit titanium oxide films at different power supply driving frequencies. A home-made large area low pressure DBD reactor was applied, characterized by the simplicity of the experimental set-up and a low consumption of feed gas and electric power, as well as being easy to operate. Atomic force microscopy, scanning electron microscopy, energy dispersive spectroscopy, and contact angle measurements have been used to characterize the deposited films. Experimental results show all deposited films are uniform and hydrophilic with a contact angle of about 15°. Compared to titanium oxide films deposited in $TiCl_4/O_2$ gas mixtures, those in $TiCl_4/O_2/N_2$ gas mixtures are much more stable. The contact angle of titanium oxide films in $TiCl_4/O_2/N_2$ gas mixtures with the addition of 50% N_2 and 20% $TiCl_4$ is still smaller than 20°, while that of undoped titanium oxide films is larger than 64° when they are measured after one week. The low-pressure $TiCl_4/O_2$ plasmas consist of pulsed glow-like discharges with peak widths of several microseconds, which leads to the uniform deposition of titanium oxide films. Increasing a film thickness over several hundreds of nm leads to the film's fragmentation due to the over-high film stress. Optical emission spectra (OES) of $TiCl_4/O_2$ DBD plasmas at various power supply driving frequencies are presented.

Keywords: dielectric barrier discharge, titanium oxide film, hydrophilic

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(Some figures may appear in colour only in the online journal)

1 Introduction

Titanium oxide films have attracted a great deal of interest as a photocatalyst [1]. When ultraviolet (UV) light energy higher than the band-gap of titanium oxide is used, inter-band transition for titanium oxide films can be induced, resulting in the generation of electron and hole pairs. Such excited electrons or holes may generate some kinds of radicals or ions, which can decompose organic compounds adsorbed on the titanium oxide film surface [2]. In addition, much attention has been devoted to its superhydrophilicity. The water contact angle of titanium oxide films decreased to almost 0° after UV illumination in air [3]. Titanium oxide films have been successfully synthesized by using the reactive magnetron sputtering technique [4−7], radio frequency (RF) plasmas [8−10], and microwave (MW) plasmas [11].

Dielectric barrier discharges (DBDs) may be used to produce non-equilibrium plasmas around atmospheric pressure [12,13]. DBDs are characterized by the presence of one or two layers of insulator between two electrodes. The experimental set-up is relatively simple and easy to operate. Atmospheric pressure DBDs have been used to deposit fluorocarbon films by Vinogradov et al [14,15]. Plenty of dust-like particles on the film surface were observed, which was presumably due to filament-like discharge pulses statistically well-distributed in atmospheric pressure DBD plasmas. Di et al. reported that TiO_2 photocatalytic films were successfully fabricated in the presence of $TiCl_4$ and excess O_2 by using a wire-to-plate atmospheric-pressure volume-DBD, the tuning effect of the N_2 content on the deposition rate, particle size and photocatalytic activity of the as-deposited TiO_2 films has also been investigated [16].

Recently, we have used low-pressure DBD plasmas to deposit diamond-like carbon films [17−19], fluorocarbon films [20,21], silicon oxide films [22] and amorphous carbon nitride films [23,24]. Also, DBDs have been applied to the plastic surface modifications [25]. The low-pressure DBD plasmas were found to contribute to the uniform deposition of various thin films with extremely low surface roughness. This DBD-induced deposition technique has many advantages, including the simplicity of experimental set-up and a low consumption of feed gas and electric power. For example, our previous investigation of film surface modifications by DBD plasmas showed that the power densities of 0.022-0.037 W/cm^2 using low DBD plasmas are several orders lower than 100 W/cm^2 from MW plasma jets [26], 8 W/cm^2 from surface-wave plasma [27], and 0.13-0.27 W/cm^2 from RF plasma [28]. Additionally, to produce DBD plasma, a common mechanical pump is required, without any expensive and complex vacuum systems. Also, the high intensity electromagnetic noise does not need shielding, which is usually generated in RF and MW plasmas.

This study focuses on the deposition of titanium oxide thin films by using low-pressure DBDs with $TiCl_4/O_2/N_2$ mixtures. In our work, cheap and non-toxic N_2 gas is used as the precursor rather than other organic precursors. Though the N_2 molecules are stable at room temperature and need enough energy to be excited or decomposed to active N species, while the electron energy in low pressure DBD plasmas is much larger than that in atmospheric pressure at room temperature, which will be beneficial for active N species generation. Atomic force microscope (AFM), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), and contact angle measurements are used to characterize the deposited films. Changes in the deposition rate, the chemical compositions and surface roughness for films deposited with different discharge parameters are reported. Optical emission spectra (OES) of $TiCl_4/O_2$ DBD plasmas at various power supply driving frequencies (f) are presented, and the relationship between the gas-phase diagnostics and film properties is discussed.

2 Experiment

2.1 Titanium oxide films deposition

The vacuum chamber for generating DBD plasmas is schematically illustrated in Fig. 1 [25]. The discharge chamber is pumped with a mechanical pump. When the chamber was evacuated to a pressure of 0.1 Pa, a high purity mixture gas of $TiCl_4$ (99.99%) and O_2 (99.99%) or N_2 (99.99%) was introduced. During film deposition, the total discharge pressure was maintained at 150 Pa. The monomer pressure was monitored with an MKS Baratron capacitance manometer. The gas spacing between the glass dielectric and the ground electrode was kept constant at 4 mm. The peak-to-peak voltage and driving frequency of this AC power supply was kept at

20 kV and at the range of 1-7 kHz, respectively. The glass and silicon (100) substrate was placed on the top of the ground electrode and the deposition time was kept for 1 min. The glass samples were divided into several pieces for the investigation of their contact angles after exposure in air for several days.
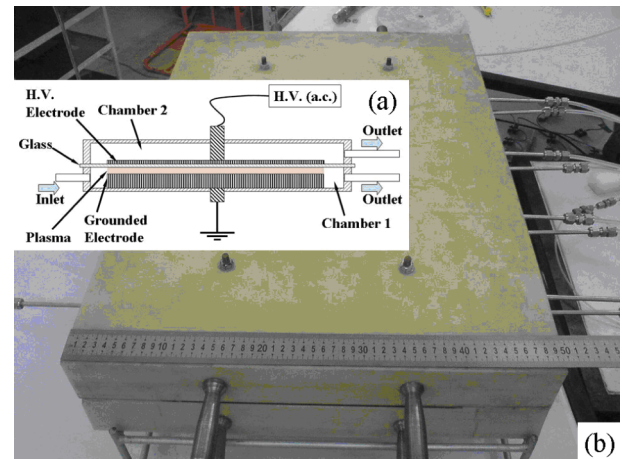

Fig.1 Schematic diagram of the low-pressure DBD plasma reactor for film deposition and optical emission spectroscopy studies

2.2 Titanium oxide films characterization

SEM (HITACHI S-4800) was utilized to measure the thickness of titanium oxide films. The SEM was carried out mainly on specimen cross sections that were produced by flexing to fracture the titanium oxide-coated Si crystal specimens. Deposition rates were calculated by dividing the film thickness by the deposition time. EDS was used to measure the film compositions. Contact angle measurements of the films immediately followed plasma deposition. To further investigate the stability of the films, contact angle measurements of different samples were taken after several days. Static contact angles for water were measured using the sessile drop method with a contact angle goniometer (Phoenix 300, SEO). Measurements were taken at ambient temperature after 5 μL drops were applied to the surface and the needle tip removed from each drop. For each sample, three drops were placed at different locations on the sample surface. Reported contact angles are the average of these measurements for each sample. AFM measurements were carried out in the tapping mode with model Dimension 3100 from Digital Instruments. The silicon tip with a tip radius typically in the range of 5-10 nm was used to conduct these measurements. Surface root-mean-square (RMS) roughness values were derived from the AFM images.

2.3 OES diagnostics of $TiCl_4/O_2$ dielectric barrier discharge plasmas

OES spectra were collected to identify excited state species using an Ocean Optics QE65000 with its reso-

lution of 0.10 nm. One fiber optic cable, connected to a charge coupled device (CCD) detector, was used to collect emission over a wavelength range of 200 - 900 nm. The photofiber probe has a 600 μm entrance aperture through which the emitting light was picked up. The integration time of this spectrometer is 800 ms, which efficiently avoids the effect of the periodic on - off discharges on the signals measured. A dark spectrum was subtracted from each spectrum.

3 Results and discussion

3.1 Titanium oxide films deposition rate and their composition analysis by SEM

Fig. 2 is an SEM micrograph of a cross section of a fractured titanium oxide film deposited on a silicon substrate at a TiCl$_4$ fraction of 20% and f=1 kHz. The film thickness is approximately 390 nm. The deposition rates of titanium oxide films at various TiCl$_4$/O$_2$ ratios and driving frequencies are listed in Table 1. The deposition rate of titanium oxide films at the TiCl$_4$ fraction of 20% decreases from 390 nm/min to about 110 nm/min while f increases from 1 kHz to 4 kHz and 7 kHz. The film deposition rate obviously increases with 57 nm/min to 1600 nm/min when the TiCl$_4$ fraction is varied from 5% to 40%. EDS measurements show that titanium oxide films are composed of Ti, O and Cl (Table 1). Increasing TiCl$_4$ fraction from 10% to 40% leads to a significant increase in the Ti content in deposited films, which is consistent with the variation of the deposition rate with TiCl$_4$ fraction. EDS measurements were also investigated on the titanium oxide films deposited in TiCl$_4$/O$_2$/N$_2$ gas mixtures. Similar to Di's research work on element analysis by the XPS method, no N element was found in the surface or cross section of the as-deposited titanium oxide films [16]. On one hand, the N content in the titanium oxides films was lower and under the detection limitation of the EDS method. On the other hand, as suggested by Di et al. that N$_2$ molecules thus play a tuning effect on the discharge, they found that with the increase in the N$_2$ content, the vibrational temperature of N$_2$ increased, the electron excitation temperature decreased, and there was no obvious change in the gas temperature. But the addition of N$_2$ resulted in the changing of the TiO$_2$ de-

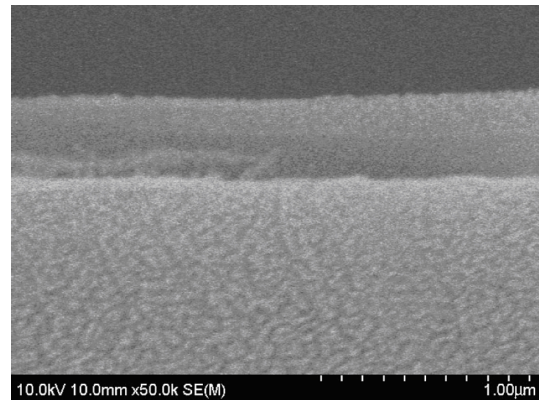position rate, particle size, and photocatalytic activity of the as-deposited TiO$_2$ film [16].

Fig.2 SEM micrograph of a cross section of a fractured titanium oxide film. Film was deposited on a silicon substrate at TiCl$_4$ fraction of 20% and f=1 kHz

3.2 Morphology analysis of titanium oxide films by AFM

Fig. 3 shows the typical AFM images for titanium oxide films deposited at the TiCl$_4$ fraction of 20% and f=1 kHz, 4 kHz, and 7 kHz. The AFM images for films deposited at f= 4 kHz and 7 kHz are extremely smooth, compared to the one for the film deposited at f=1 kHz. The nanostructures with decorative pattern may be observed at the surface of the titanium oxide film deposited at f=1 kHz. RMS roughness values for all deposited films are listed in Table 1. The AFM images for titanium oxide films deposited at f=4 kHz and TiCl$_4$ fractions of 5%, 10%, and 40% are shown in Fig. 4. The titanium oxide films deposited at TiCl$_4$ fractions of 5% and 10% are relatively smooth compared to the one deposited at the TiCl$_4$ fraction of 40%. The rough surface for the titanium oxide film obtained at the TiCl$_4$ fraction of 40% can result from the film's fragmentation. The RMS values are well related to the film deposition rate or film thickness. The RMS value significantly increases when the film thickness is larger than several hundreds of nanometers, indicating the titanium oxide film cracks due to a high film stress. However, when the film thickness is lower than $\sim$100 nm, the deposited titanium oxide films exhibit a uniform surface structure and an extremely low surface roughness.

Table 1. Deposition rates, RMS roughness, and Ti/O/Cl ratios for titanium oxide films deposited in TiCl$_4$/O$_2$ DBD plasmas

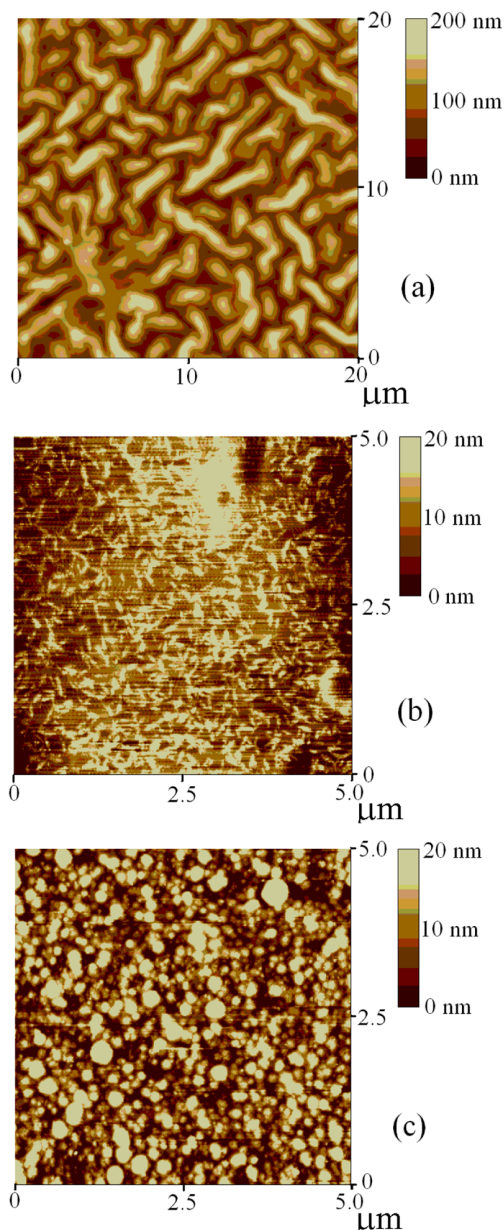| Frequency (kHz)	TiCI$_4$/O$_2$ (Pa)	Deposition rate (nm/min)	RMS roughness (nm)	Contact angle (°)	Ti/O/CI atom %
1	30/120	388±16	36.2±1.0	8.7	10.7/84.8/4.5
4	8/142	57±1	2.4	–	–
4	15/135	75.2	2.9	8.9	12.7/84.4/2.9
4	30/120	112	8.5±2.2	7.8	19.3/64.7/16.0
4	60/90	1600±420	338.8	21.0	23.8/61.6/15.2
7	30/120	108	8.8	8.5	17.1/67.2/15.7

Fig.3 Typical AFM images for titanium oxide films deposited at $TiCl_4$ fractions of 20% and (a) f=1 kHz, (b) f=4 kHz, and (c) f=7 kHz

3.3 The hydrophilicity of the deposited titanium oxide films dependence on exposure time

Fig. 5(a) shows contact angles for the deposited titanium oxide films with different $TiCl_4$ contents in $TiCl_4/O_2$ mixtures varied with exposure time. The newly deposited titanium oxide films are hydrophilic with contact angles of about 10°-17° with different $TiCl_4$ contents. But the hydrophilicity of the samples varied largely in two days. The contact angles increased up to 62°-84° when they were measured on the second day. The values are larger than those over pure Si substrate. SEM characterization of the deposited TiO_2 film after exposure to the air for more than one day

shows that the films are cracked, especially for TiO_2 films with large thicknesses. Generally, the RMS value of the surface roughness of the cracked film was larger than those without cracking. So it can be easily seen that the decrease of the hydrophilicity of the films may be related to the large roughness of the surface. By further increasing the exposure time up to more than one week, the contact angles of the deposited films increased slowly. The smallest contact angle in the deposited titanium oxide films was 66° for the one with 10% $TiCl_4$ when they were measured on the tenth day.
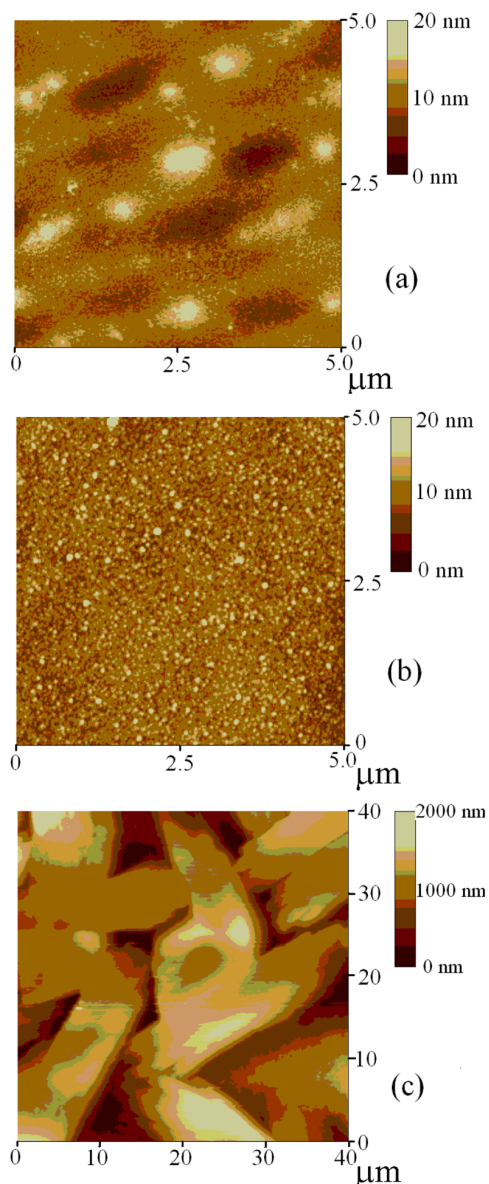

Fig.4 Typical AFM images for titanium oxide films deposited at f=4 kHz and $TiCl_4$ fractions of (a) 5%, (b) 10%, and (c) 40%

On the mechanism of the hydrophilic property of TiO_2, the most acceptable explanation is that there is the formation of an oxygen vacancy at the TiO_2 surface. These vacancies can adsorb OH to induce the hydrophilicity [29−31].
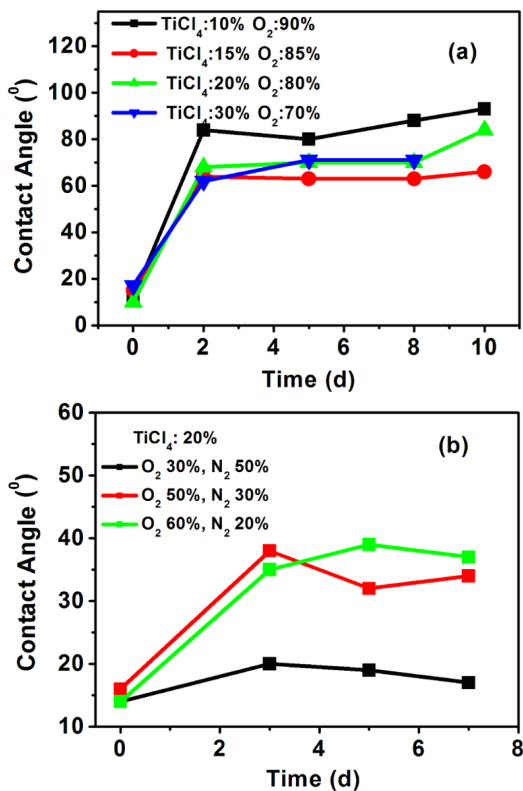
Fig.5 Contact angles for deposited titanium oxide films varied with exposure time. (a) In $TiCl_4/O_2$ mixtures with different $TiCl_4$ contents, (b) $TiCl_4(20\%)/O_2/N_2$ mixtures with different N_2 content

Fig. 5(b) shows the contact angles for deposited titanium oxide films varied with exposure time in $TiCl_4/O_2/N_2$ mixtures with O_2 as a balance gas, 20% $TiCl_4$ and different N_2 contents. The contact angles for the deposited titanium oxide films in $TiCl_4/O_2/N_2$ mixtures are less than 16° and nearly the same as those undoped titanium oxide films when they are measured immediately after the deposition. Also, when they are exposed to the air for several days, the contact angles varied similarly. But the values are less than those without N_2 addition. Those deposited with N_2 content of 50%, 30%, and 40% are 20°, 38°, and 35°, respectively. Especially for the one deposited with a N_2 content of 50%, the value is still less than 20° when it is determined on the seventh day. It is clearly indicated that in 20% $TiCl_4$ content plasmas, the higher N_2 content will lead to a more stable hydrophilicity of the deposited titanium oxide films in $TiCl_4/O_2/N_2$ mixtures. The relationship between the hydrophilicity and N content in the gas mixtures and the crystal structures of the as-deposited films is under investigation.

3.4 Discharge characteristic of $TiCl_4/O_2$ DBDs

Fig. 6(a) shows the applied voltage and current waveforms obtained at the $TiCl_4$ fraction of 20% and f=1 kHz. The current directions (positive or negative) and the average amplitude of the current pulses are different in the voltage-rising and voltage-falling half-cycles. The differences in two half-cycles are due to the different mobility of electrons and ions on the glass surfaces [32]. For clarification, the extended voltage and current waveforms are shown in Fig. 6(b). The pulsed breakdowns produce pulsed currents with peak values of about $0.01\ mA/cm^2$, which are within the range of glow discharge. Due to the nearly uniformly distributed current pulses, it can be concluded that the low-pressure DBDs consist of glow-like and large-area uniform (along the whole electrode) single breakdowns with peak widths of several microseconds. This characteristic contributes to the uniform deposition of titanium oxide films.
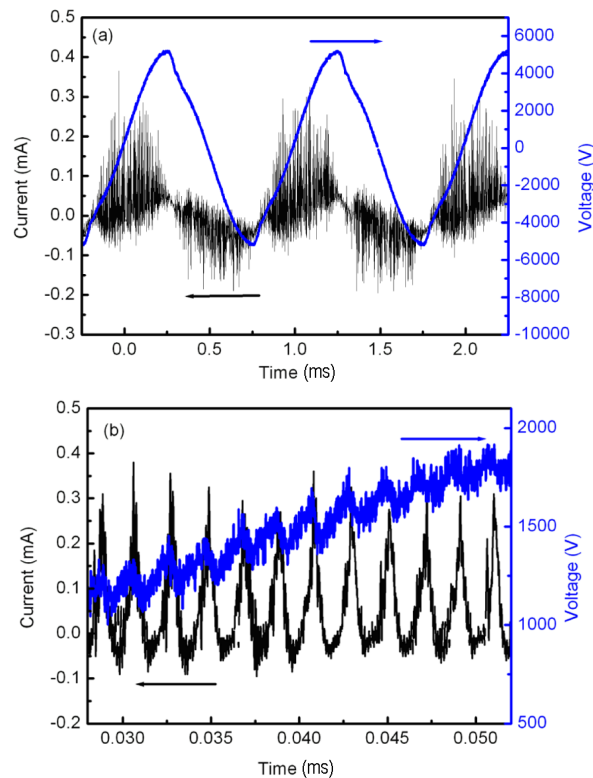
(a) 0.5 ms/div, (b) 0.005 ms/div

Fig.6 The applied voltage and current waveforms of barrier discharge plasmas obtained at $TiCl_4$ fraction of 20% and f=1 kHz

3.5 Active species in $TiCl_4/O_2$ DBDs

Fig. 7 shows the typical OES spectra of $TiCl_4/O_2$ DBD plasmas generated at a $TiCl_4$ fraction of 20% and f=1 kHz, 4 kHz, and 7 kHz. The OES spectra are dominated by the O (777 nm) emission peak. No emission peaks for titanium- or chlorine-containing species were observed. The O emission intensity increases with the driving frequency due to the increasing discharge power. The O atoms produced in the gas phase may play a crucial role in oxidizing $TiCl_4$ molecules at the film surface and contribute to film growth. However, $TiCl_4$ or Ti-containing species can control the film growth since the film growth rate significantly increases with $TiCl_4$ fraction (Table 1).
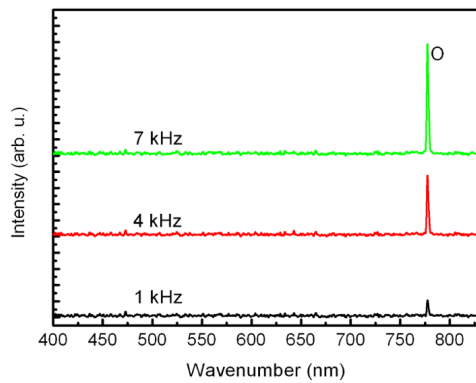
Fig.7 Typical OES spectra of $TiCl_4/O_2$ DBD plasmas generated at $TiCl_4$ fraction of 20% and f=1 kHz, 4 kHz, and 7 kHz

4 Conclusion

Titanium oxide films with uniform surface structures have been synthesized with $TiCl_4/O_2$ or N_2 DBD plasmas. The effects of gas compositions and the DBD power supply driving frequency on the deposition of titanium oxide films were studied. All deposited films were uniform and hydrophilic with a typical contact angle of about 15°; however, when they were exposed in the air, the contact angles varied to different degrees. The films deposited in 20% $TiCl_4$, 50% N_2, and 30% O_2 mixtures were much more stable. The contact angle was still less than 20°, even when it was exposed in the air for seven days. Simultaneous measurements of applied voltage and discharge current indicate that the $TiCl_4/O_2$ plasmas consist of pulsed glow-like discharges with peak widths of several microseconds, which leads to the uniform deposition of titanium oxide films. When the film thickness is larger than several hundreds of nm, the titanium oxide films crack due to the over-high film stress. OES spectra are dominated by the O (777 nm) emission peak, indicating O atoms play a crucial role in oxidizing Ti-containing species at the depositing surface. The results also indicate that the film growth rate can be controlled by the concentration of Ti-containing species in the gas phase.

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