

Photonic molecular effects associated to the sputtering process in a glow discharge optical emission spectrometer

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Spectral emission of a Xenon discharge in the presence of NaCl powder is strongly modified and dominated by the XeCl excimer band at 308 nm. Materials introduced in gas electrical discharges interact with the reactive species produced in the plasma: electrons, ions and metastable atoms. In this paper, the influence of ions and metastable atoms of a capacitive RF Xenon discharge plasma (20W, 30MHz) 5 Torr on the structure of a NaCl powder introduced in the discharge has been investigated.

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1. Introduction

In radio-frequency (rf) Glow Discharge Optical Emission Spectroscopy (GDOES) systems conductive and nonconductive materials can be sputtered and then excited in the RF glow discharge plasma, which permits elemental analysis.

The sputtering process occurring at the cathode surface from positive ions bombardment leads to different surface modifications. We have studied the case of NaCl salt in Xe discharge. Emission spectrum of the xenon discharge in the presence of NaCl powder is dominated by the XeCl excimer band at 308 nm. This opens wide possibilities for laser technology. At the same time, the evolution of the salt with the sputtering in terms of stoichiometry and surface properties is of high interest, since this may influence the plasma dynamics as it is shown in this paper.

A well suited method for analyzing surface modifications of the NaCl is X-ray photoelectron spectroscopy (XPS), due to the small photoelectron escape depth [1]. X-ray photoelectron spectroscopy on NaCl was discussed more than three decades ago [2] with emphasis on valence band and shallow core levels. More recently, Filipponi et al. [3] reported detailed studies of the Na 1s shake-up satellites. Na 1s and Cl 2p spectra may be found in databases [4], but with no assignment of the various components. In the present work, we studied in more detail the XPS spectra of both genuine and plasma treated NaCl.

2. Experimental

The experimental set-up is presented in Fig. 1.

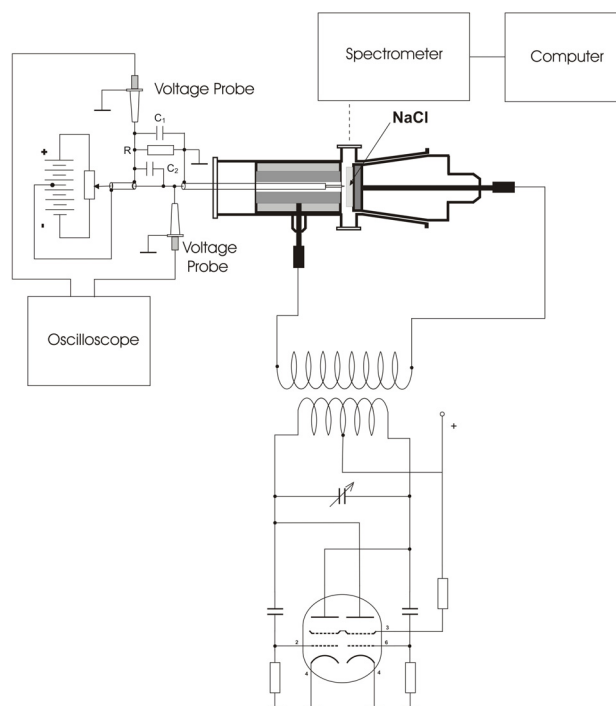


Fig. 1. Experimental set-up.

The glass discharge tube used in our experiment is shown in Fig. 1. The samples are attached by vacuum grease to the cathode - disc of 10 mm diameter fixed to a glass stopper which can be easily removed to allow easy sample change.. The anode is a copper cylinder of 15 mm length and 4 mm diameter placed in front of the cathode. The capacitive discharge Xenon plasma is generated at 5 Torr with a homemade RF generator working in the power range 0- 40 W and 30 MHz frequency [5]. The sample is pure NaCl salt (Aldrich, 99, 9 %). Spectral investigations are made with a SHAMROCK SR-303i spectrograph and ICCD detector, with 0.1 nm resolution.

3. Results and discussion

In Fig. 2 is presented the Xe spectrum obtained in this configuration. The plasma parameters, were measured with a Langmuir probe using an electric circuit adapted for RF discharges [6] (Fig. 1). The electronic temperature is 2.64 eV and the electron density $1.87 \times 10^{10} / \text{cm}^3$.

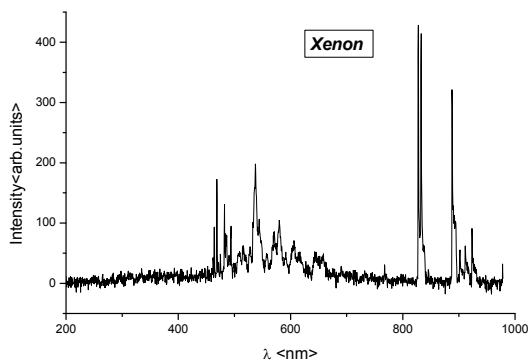


Fig. 2 Xenon spectrum obtained in the RF cell discharge.

The spectrum is dominated by the very intense lines of Xenon at 823.1 nm and 828.0 nm. When NaCl sample is introduced in the Xenon discharge [5], the emission lines of atomic and ionic Xenon are strongly reduced as it can be observed in Fig. 3 and a large band at 308 nm appears and dominates the entire spectrum.

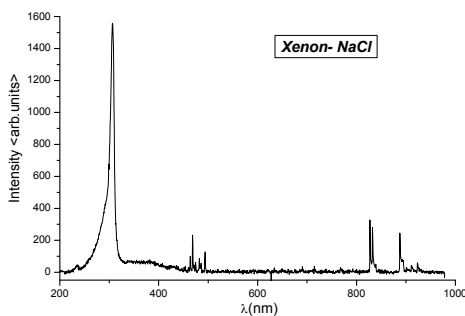


Fig. 3. Xenon spectrum in the presence of NaCl.

The appearance of the excimer transition band at 308 nm can be explained by the formation during the RF discharge of the bound excited state of XeCl dimer molecule.

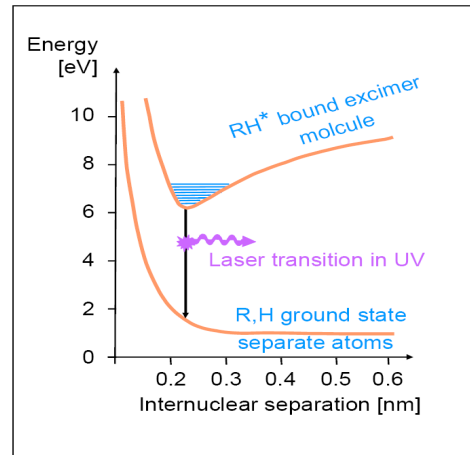


Fig. 4. Energetic levels of XeCl dimer molecule.

Before we can propose a generation mechanism of the excimeric band at 308 nm, we need to take into account the energetic diagrams of Xenon and of NaCl. Xenon has an ionization potential at 12.13 eV and a metastable level at 8.31 eV. The energetic diagram of NaCl is presented in the Fig. 5.

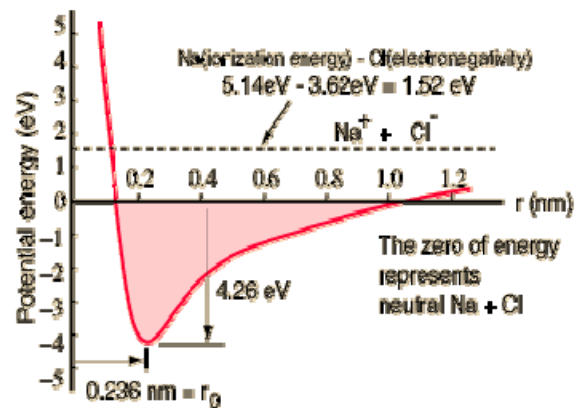
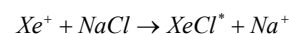


Fig. 5. Energetic diagram of NaCl.

The photonic effect observed (in Xe - NaCl mixture) in the vicinity of the cathode in a GD type plasma, namely the appearance of the excimer band at 308 nm, may result from the following process

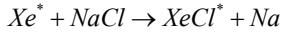


which is energetically possible:

$$E(\text{Xe}^+) + E(\text{Na}^+) + E(\text{Cl}^-) - D(\text{NaCl}) = 12.13\text{eV} + 5.14\text{eV} - 3.62\text{eV} - 4.23\text{eV} = 9.42\text{eV}$$

$$E(\text{Na}^+) + E[\text{XeCl}^*(308\text{ nm})] = \\ = 5.14\text{ eV} + 4.03\text{ eV} = \mathbf{9.17\text{ eV}}.$$

The slow disappearance of xenon atomic lines may be explained if atomic metastables are involved in this photonic effect and react as follows:



a process which is also energetically possible

$$E(\text{Xe}^*) + E(\text{Na}^+) + E(\text{Cl}^-) - D(\text{NaCl}) = \\ = 8.31\text{ eV} + 5.14\text{ eV} - 3.62\text{ eV} - 4.23\text{ eV} = \mathbf{5.6\text{ eV}}$$

$$E(\text{Na}) + E[\text{XeCl}^*(308\text{ nm})] = \\ = 0\text{ eV} + 4.03\text{ eV} = \mathbf{4.03\text{ eV}}.$$

This means that metastable atoms produced in glow discharge plasmas, are involved not only in ionization processes [8], but also in sputtering processes.

The dominant XeCl excimer band at 308 nm emitted in Xe discharge in the presence of NaCl powder opens wide possibilities for building cheap and ecological UV lamps for industrial processing and medicine [9].

At the same time, the evolution of the salt in terms of stoichiometry and surface properties is of high interest, since it influences the plasma dynamics.

X-ray photoelectron spectroscopy on NaCl was reported more than three decades ago [2] with emphasis on valence band and shallow core levels. More recently, Filipponi et al. [3] reported detailed studies of the Na 1s shake-up satellites. Na 1s and Cl 2p spectra may be found in databases [4], but with no assignment of the various components.

In the present work, we studied in more detail the XPS spectra of both, genuine and 10 minutes plasma treated NaCl sample. The plasma treated NaCl sample was removed carefully from the surface of cathode and moved quickly to the XPS chamber.

X-ray photoelectron spectra were recorded by using a VG ESCA Mk-II installation, with Al K_{α} radiation (1486.7 eV), 100 mm radius hemispherical electron energy analyzer operating with pass energy of 50 eV. The base pressure was in 10^{-9} hPa range; a Specs flood gun operating at 3 V/0.3 mA was used to achieve charge compensation at surface; core levels electron distribution curves (X-ray photoelectron spectrum) were calibrated between samples by assigning the C 1s peak from the inherent contamination layer to 285 eV [10].

Data analysis was performed by using Voigt profiles and their integrals accounting for the inelastic background, as derived in [11]. As in [10, 12], it is supposed that each line has its own associated inelastic background and the relative amplitude of the background to the line's integral amplitude is a sign of the localization of the atomic species which has photo emitted with respect to the sample. A

very weak inelastic background amplitude is a sign of the localization near to the surface.

The Na 1s, Cl 2p, and O 1s X-ray photoelectron spectra are shown in Figs. 6, 7 and 8, respectively - for both genuine and plasma treated samples. An approximate stoichiometry of $\text{NaCl}_{0.89 \pm 0.01}$ is found for the plasma treated sample, by using common databases and calibrations. Surface Na atoms which react with oxygen instead of chlorine are identified, and surface oxygen atoms reacting with sodium are also identified Fig. 8. Following the discharge, the Na-O complexes decrease considerably, as is shown by both Na 1s, Fig. 6 and O 1s, Fig. 8b spectra. Also, interstitial water is shown to decrease after discharge, whereas O-Cl coordinations are still present, in smaller quantity (about one third).

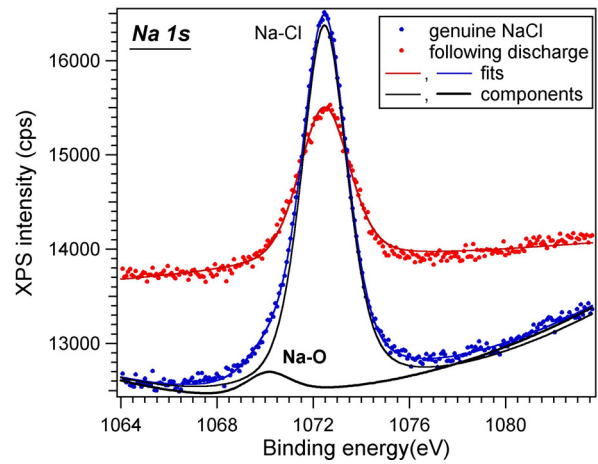


Fig. 6. Na 1s EDC before and after discharge.

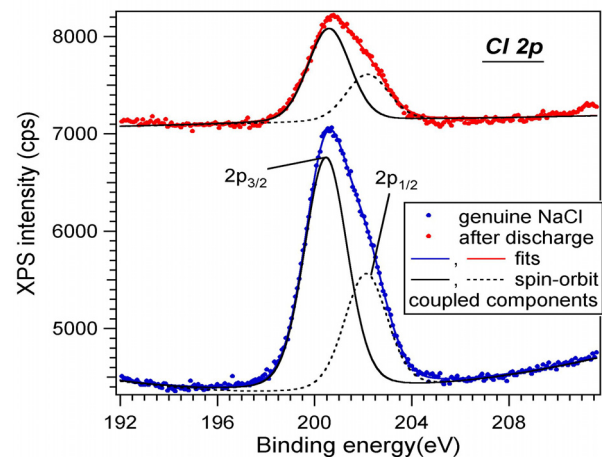


Fig. 7. Cl 2p EDC before and after discharge.

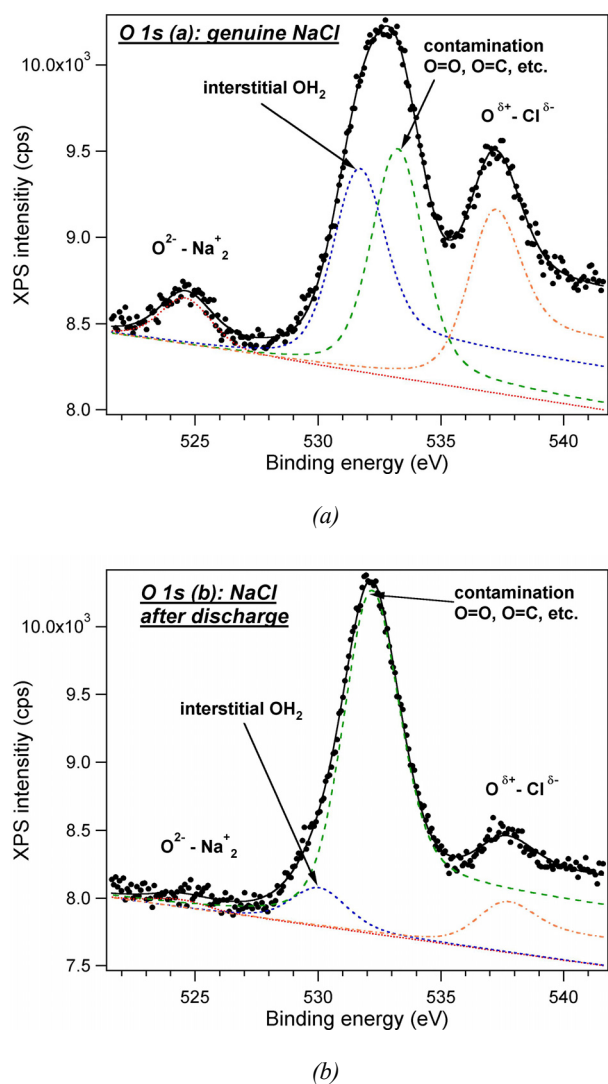


Fig. 8. O 1s EDC (a) before discharge and (b) after discharge.

Consequently, we identified:

(i) presence of Na-O bonds in the genuine salt at the surface and disappearance of these bonds following treatment;

(ii) drying of the sample (eliminating the interstitial water) following the discharge;

(iii) presence of oxygen-chlorine coordination, which does not disappear completely following the discharge.

Conclusions

In conclusion we reported a strong emission of XeCl excimer band at 308 nm in a RF- GD source with Xe buffer gas and NaCl target accompanied with strong quenching of Xe levels. These phenomena are important to explain optical and MS spectra in GD experiments and for developing new excimer laser configurations. A coaxial electrode configuration as described in [13] for laser emission at 308 nm will be the subject of a future development.

References

- [1] S. Hüfner 2003 Photoelectron spectroscopy, Springer, Berlin.
- [2] S. P. Kowalczyk, F. R. McFeely, L. Ley, R. A. Pollak, D. A. Shirley, *Phys. Rev. B* **9**, 3573 (1974).
- [3] A. Filipponi, S. Di Nardo, M. Passacantando, L. Lozzi, S. Santucci, and P. Picozzi, *Phys. Rev. B* **48**, 13430 (1993).
- [4] B.V. Crist Handbooks of Monochromatic XPS Spectra **1-5**, XPS International LLC, Mountain View (2004)
- [5] C. Diplasu, A. Surmeian, A. Groza, M. Ganciu, I. I. Popescu, Proceedings of ESCAMPIG, Lecce 2006.
- [6] C. Diplasu, A. Surmeian, H. Fujita; *J. Optoelectron. Adv. Mat.* **7**, 2397 (2005).
- [7] A. M. Boichenko, A. M. Prokhorov, *Quantum Electronics* **29**, 1001 (1999).
- [8] A. Surmeian, C. Diplasu, A. Groza, M. Ganciu, P. Bellenger, A. Tempez, P. Chapon; *Anal. Bioanal. Chem.* **388**, 1625 (2007).
- [9] U. Kogelschatz, *Pure and Applied Chem.* **62**, 1667 (1990).
- [10] O. Pana, C. M. Teodorescu, O. Chauvet, C. Payen, D. Macovei, R. Turcu, M. L. Soran, N. Aldea, L. Barbu *Surf. Science* **601**, 4352 (2007).
- [11] C. M. Teodorescu, J. M. Esteva, R. C. Karnatak, A. El Afif *Nucl. Instrum. and Methods in Phys. Research A* **345**, 141 (1994).
- [12] D. Luca, C. M. Teodorescu, R. Apetrei, D. Macovei, D. Mardare *Thin Solid Films* **515**, 8605 (2007).
- [13] M. Ganciu, A. Surmeian, C. Diplasu, I. Chera, G. Musa, I. I. Popescu, *Opt. Commun.* **88**, 381 (1992).

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