Study of processes in glow discharge optical emission spectrometry in Ne and Ar plasma for the determination of light elements with high ionization potential and excitation energy such as oxygen and fluorine in conducting materials

#optical emission spectrometry *#neon* *#direct current discharge* *#oxygen* *#pulsed glow discharge* *#fluorine* *#radio-frequency discharge* *#argon*

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Highlights

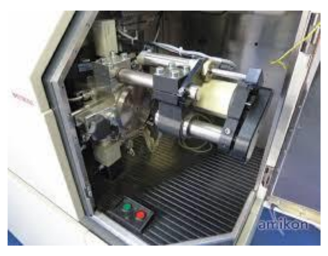
1. Different types of discharge (radio-frequency, direct current and pulsed direct current glow discharge) were compared for the determination of F and O.
2. The effectiveness of pulsed direct current was shown for excitation of F and O.
3. The process of evaporation and secondary electron emission in fluoride samples was described.
4. A memory-effect for fluorine was observed.
5. The efficiency of Ne discharge was confirmed for the determination F.

Introduction

The analysis of light elements, such as fluorine and oxygen, in solid materials is a particularly difficult task. However, in recent years, there were reports about application of glow discharge for determination of light elements [1-5]. For this reason the comparison of different types of discharge (radio-frequency (RF), pulsed direct current (PDC) and continues direct current (DC) glow discharge) and gases (Ne and Ar) for excitation of fluorine and oxygen is the main goal in this work.

Different approaches can be applied for efficient excitation and ionization of light elements with high excitation and ionization potential: 1) using discharge gases with a potential of metastable atoms higher than the potential of elements, or small additives of these gases in the main discharge gas [1-3], 2) using the mechanism of electron excitation instead of Penning excitation in glow discharge [3-5]. The excitation energy of argon metastable levels is 11.55 eV and 11.72 eV, which are not enough for excitation of F (14.50 eV). Oxygen has excitation levels (9.52 eV for 130 nm and 10.74 eV for 777 nm) lower than the argon metastable levels, however a better detection limit is of interest. For this reason, we used the neon discharge gas (levels of neon metastables are 16.62 eV and 16.71 eV) for effective determination of F and O. Also, the approach 2) using different discharge types was applied.

Materials and methods

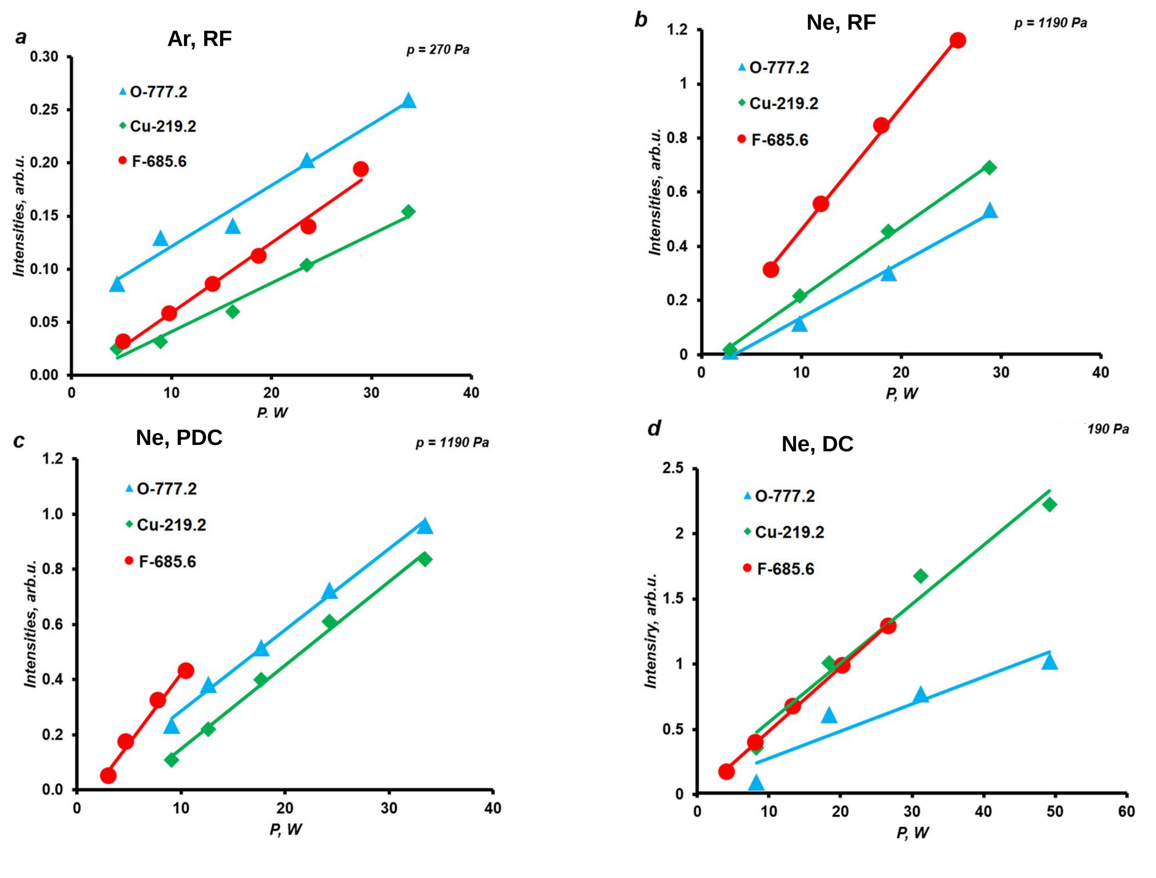


GDA750HR with CCD and PMT detectors (Spectruma Analytik GmbH, Hof, Germany)

Composition of calibration specimens.

№	Cu, mass %	F, mass %	O, mass %	Ca, mass %
1	96.77	1.57	0.00	1.65
2	93.75	3.04	0.00	3.21
3	90.91	4.42	0.00	4.67
4	98.98	0.00	1.02	0.00
5	98.14	0.00	1.86	0.00
6	97.42	0.00	2.58	0.00

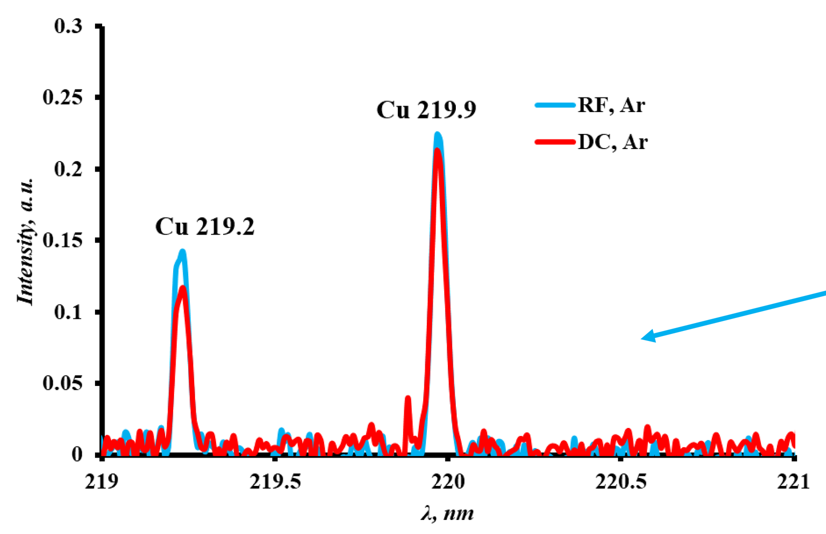
Comparison condition: same power, same pressure



Parameters used for determination of oxygen and fluorine in different types of discharge.

Discharge Gas	Ar			Ne		
Method	Cont. DC	Cont. RF	PDC	Cont. DC	Cont.RF	PDC
Element	O / F					
Power (sample 4-6), W/ Power (sample 1-3), W	30/30	30/30	30/17	30/30	30/30	30/7
Pressure, Pa	270			1190		
Frequency, kHz	-	-	6	-	-	4
Pulse duration, µs	-	-	4	-	-	4

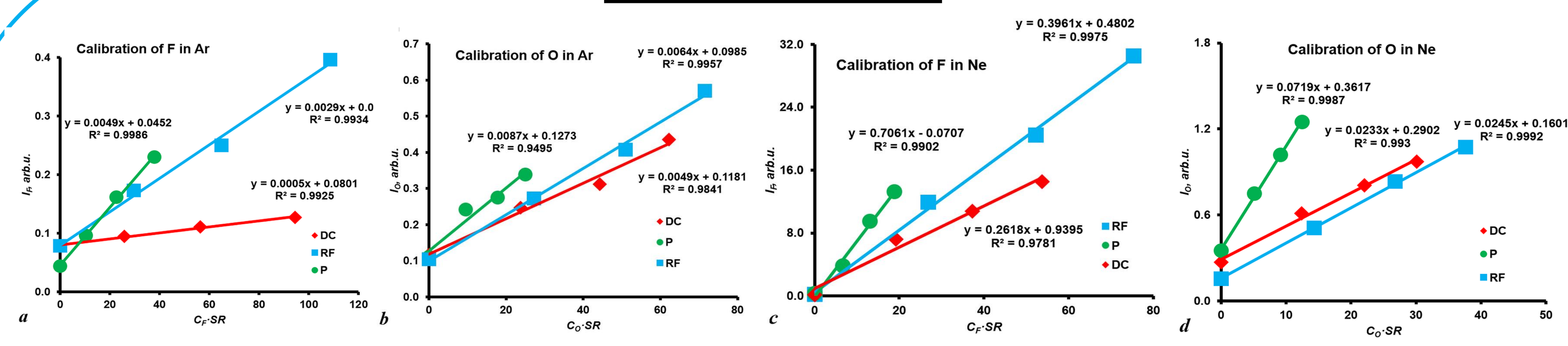
RF and DC



Spectrum of sample №1 in DC and RF Ar discharge

For the determination of power in RF discharge normalization on sputtering rates was used.
Firstly, the same voltage and pressure were set.
Secondly, anode voltage of RF generator was selected so that the same intensity of the Cu spectral lines was achieved.
After that, the sputtering rate was determined in selected conditions for a series of samples.

Calibration curves



$$\frac{R_{nm}}{R_{nm}^{DC}} = \frac{I_e \cdot SR_e^{DC}}{I_e^{DC} \cdot SR_e}$$

R_{nm} - emission yield of chosen discharge; R^{DC}_{nm} - emission yield in DC discharge; I_e – intensity of element; I^{DC}_e – intensity of element in Ar DC; SR_e – sputtering rate of sample; SR^{DC}_e – sputtering rate of sample in Ar DC.

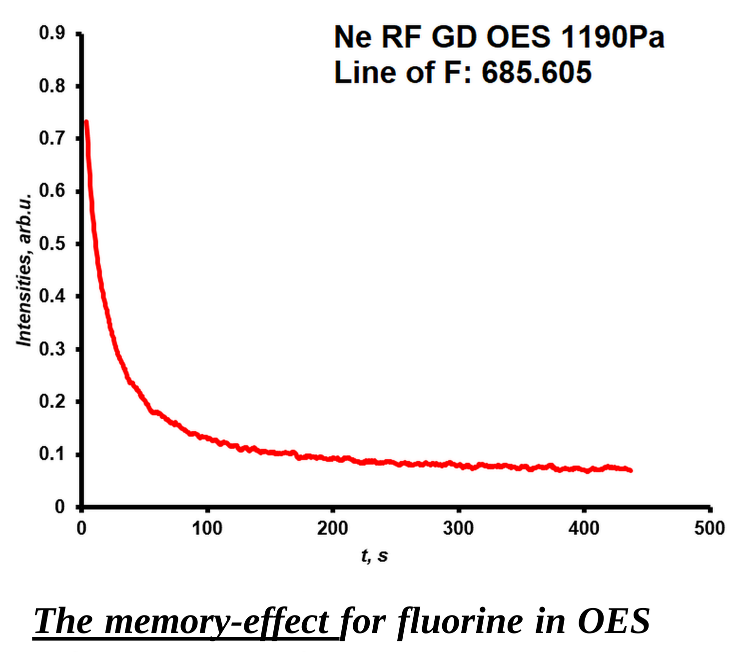
Comparison of different discharge types for the determination of fluorine and oxygen, their efficiency of emission and sputtering. All intensity values were normalized on 30W.

Sample	Discharge gas	Type of discharge	SR_O, µg/s	I_O/I_O^{DC}	R_{nm}/R^{DC}_{nm}	SR_F,µg/s	I_F/I_F^{DC}	R_{nm}/R^{DC}_{nm}
№6/№3	Ar	DC	24.1	1	1.0	24.0	1	1.0
		PDC	9.7	0.8	2.0	8.6	2	5.6
		RF	27.7	1.3	1.1	24.5	3	2.9
	Ne	DC	11.7	2.2	4.6	12.2	96	189
		PDC	4.8	2.5	12.5	4.3	104	588
		RF	14.6	2.5	4.1	17.0	217	306

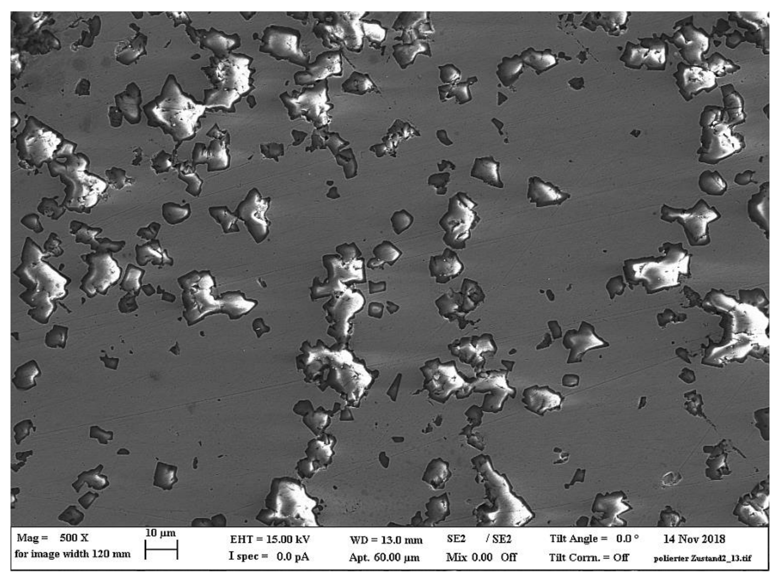
LoDs of O and F in different types of discharge

Parameters	OES					
	Cont DC		PDC		RF cont	
	Ar	Ne	Ar	Ne	Ar	Ne
LoD (O), mass %	0.5	0.23	0.4	0.20	0.6	0.21
LoD (F). mass %	1.5	0.005	0.8	0.006	1.0	0.007

Special aspects of fluorine and fluoride materials



***The memory-effect** for fluorine in OES using pure Cu in Ne RF GD as an example.*



***Evaporation effect – secondary electron emission**: SEM EDX image of №3 sample surface near the crater edge after discharge in PDC mode. (15 kV, 10 µm, 500 multiplication).*

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