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Excitation of the gas-phase selenium by electron impact[*]

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Abstract. Slow electron excitation of selenium in the gas-phase has been studied using an optical spectroscopy method. The emission spectra of selenium were recorded in the wavelength range of 200–590 nm at the incident electron energies of 20, 30 and 50 eV. In the above spectra, the molecular emissions within the wavelength range of 300–560 nm as well as the selenium atomic spectral lines were observed. The optical excitation functions for the most intense molecular emissions and atomic selenium spectral lines were measured.

1 Introduction

Selenium is a non metallic chemical element with good photovoltaic and photoconductive properties extensively used in electronics, such as photocells, light meters and solar cells. In addition, selenium is an important trace mineral, which plays an active role in many biological systems as it has toxicological and physiological effects.

Selenium is well-known to tend to form molecules Se_n ($n = 2$–8) during its evaporation, in addition the concentration of different species heavily depends on the temperature [1–3]. Unfortunately, there are few works aimed at studying the selenium vapor composition at different temperatures. The results obtained in the above works are quite controversial, that being explained by the various experimental conditions and methods of producing selenium in the gas phase. Recent results on the selenium vapor composition were obtained in [4] using a photoionization mass spectrometric method, according to which the most dominant molecules at the 510 K temperature are Se_6, Se_5, Se_2. In this work, the ionization energy of the selenium molecules have also been determined.

Little is known about the electron impact excitation of the atomic selenium and selenium molecules. The reasons for this are the complexity and temperature dependence of the selenium vapour composition. The author of [5] has investigated the dissociative excitation of the selenium atom in electron collisions with the S_2 molecule. In this work, the emission spectra within the wavelength ranges of 200–220 nm, 323–363 nm and 450–540 nm were studied and the optical excitation functions (OEF) for the 17 spectral lines were measured. As far as we know, there are no data on the selenium molecule excitation by electron impact. The aim of this work is to extend our knowledge on excitation processes taking place in the selenium vapor under the low energy electron impact.

2 Experiment

Experiment was carried out using a gas-filled cell at the incident electron current of 25 μA provided by a four-electrode gun with an oxide cathode (Fig. 1). A container with the crystalline selenium was placed in a close proximity to the cell provided with direct heating. In all our measurements, the container temperature was maintained within the 430–450 K range. To prevent selenium condensation on the electron gun and collision cell elements their temperature was kept 20–30 K above that of the selenium container. The residual gas pressure in the vacuum chamber under operating conditions did not exceed 10^{-4} Pa. A collimated electron beam (2 mm in diameter) passed the vapor-filled cell and was detected by a deep Faraday cup. The instability of the electron current having passed the collision chamber did not exceed 3%. The electron beam energy spread in vacuum was 0.4 eV (FWHM). When measuring the OEFs the electron energy was varied with 200 meV step. Radiation selected by a diffraction monochromator MDR-2 was detected by a FEU-106 photomultiplier. The single photo-electron pulses from photomultiplier were amplified, shaped by a wideband amplifier-discriminator and it entered the pulse counter via a PC interface card. In order to maintain the accuracy of measurements, when the statistical scatter of the pulses did not exceed 5–10%, the accumulation of signal at each point was carried out with an exposure of 10 to 40 s. The emission spectra in the 200–590 nm spectral region were measured with a step of 1.2 nm and 1 mm wide monochromator slit (i.e. $\Delta\lambda = 2$ nm) at fixed electron

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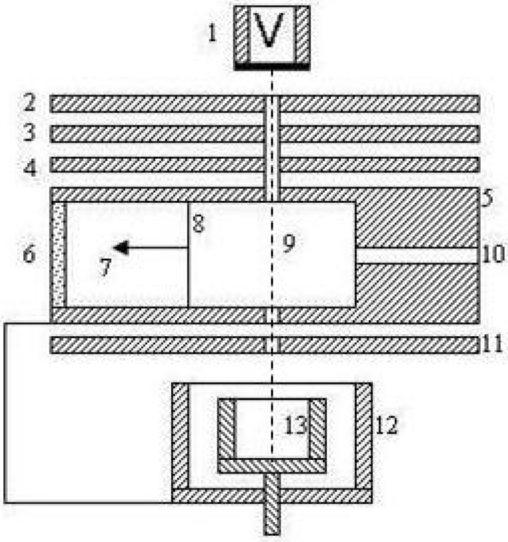

Fig. 1. The layout of a four-electrode gun: 1– oxide cathode, 2 – first anode, 3 – second anode, 4 – third anode, 5 – fourth anode, 6 – quartz window for transmitting radiation, 7 – direction of radiation to the spectral device, 8 – collision chamber, 9 – trajectory of electrons, 10 – intake of the vapor of the investigated substance, 11 – hold back anode, 12, 13 – external and internal (Faraday cup) cylinders.

energies of 20, 30 and 50 eV. The spectra were measured with a modulated electron beam, i.e. the cathode radiation was subtracted from the total signal with no taking into account the spectral sensitivity of the photomultiplier and the spectral transmission characteristics of the monochromator. One can find more detailed description on the experimental technique and method in references [6,7].

For correct interpretation of the results of measurements, calibration of the energy scale of the incident electron beam is an essential problem. Such calibration was carried out in two ways: with respect to the shift of the electron beam current-voltage-dependence at the collector as well as by a sharp maximum observed at 14.2 eV in the OEF of the nitrogen molecule second positive system ($\mathrm{C}^3\Pi_u \rightarrow \mathrm{B}^3\Pi_g$, $\lambda = 337.1$ nm) [8]. To measure this OEF the residual gas pressure in the vacuum chamber was increased by one order of magnitude for achieving the necessary concentration of the nitrogen. The energy difference between the maximum measured by us and that obtained in work [8] gives the contact potential difference.

3 Results and discussion

Figure 2 shows the selenium emission spectra measured in the wavelength range of 200–590 nm at the electron energies of 20, 30 and 50 eV. The spectra appear to be continuous in the 300–560 nm range, in addition, a number of atomic spectral lines with the maxima at 207.5 nm, 216.4 nm, 474 nm and 537 nm can be observed. The 207.5 nm and 216.4 nm spectral lines were found to be the selenium atomic resonance lines corresponding to the $4p^{43}\mathrm{P}_2$-$4p^3(^4\mathrm{S})5s^5\mathrm{S}^0_2$ and $4p^{43}\mathrm{P}_1$-$4p^3(^4\mathrm{S})5s^5\mathrm{S}^0_2$ transitions, respectively. Regarding the 474 nm and 537 nm spectral lines, they correspond to the $4p^3(^4\mathrm{S})5s^5\mathrm{S}^0_2$-$4p^3(^4\mathrm{S})6p^5\mathrm{P}_{3,2,1}$ and $4p^3(^4\mathrm{S})5s^3\mathrm{S}^0_1$-$4p^3(^4\mathrm{S})6p^3\mathrm{P}_{0,2,1}$ transitions. As seen in Figure 2, the general characteristic of the continuous emission remained almost unchanged with the incident electron energy increase, while the intensity of the spectral lines has increased significantly. This can be explained by the fact that the excitation cross sections of the spectral lines rise as a function of electron energy. We suppose that the continuous emission observed in the spectra must be produced by some of the Se_2-Se_8 molecules [5].

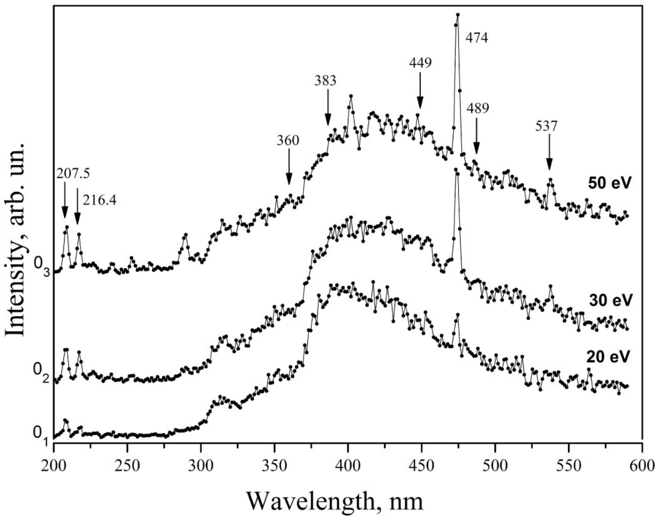

Fig. 2. Selenium emission spectra measured in the wavelength range of 200–590 nm.

Figure 3 shows the OEFs measured for the 360 nm, 383 nm, 449 nm and 489 nm spectral emissions chosen arbitrarily in the 300-560 nm wavelength range where the spectra are continuous. Note that all the OEFs have low excitation thresholds, i.e. 3.7, 3.2, 2.7 and 2.5 eV, respectively. In reference [3], it has been found that at 440 K the Se_2 molecule has the highest concentration in the selenium vapor. Thus, we can suppose that the low threshold energies of the OEFs correspond to the electron transitions in the Se_2 molecule between the ground electronic vibrational states $(^3\Sigma_g^-)$ and the first excited electronic vibrational energy levels [5]. Note that the OEF of the 489 nm spectral emission differs from the other ones in the energy region from the threshold to 10 eV. This can be explained by the overlap of the 488.7 nm intercombination atomic spectral line ($4p^{43}\mathrm{P}_1$–$4p^{41}\mathrm{S}_0$) whose excitation threshold energy (2.78 eV) lies close to that of the 489 nm emission. A number of features can be observed in the energy range of 4–15 eV that might be produced by the resonances formed due to the selenium molecule excitation.

Figure 4 shows the OEFs for the 207.5 nm, 216.4 nm, 474 nm and 537 nm spectral lines. The threshold excitation energies of these spectral lines, according to the results [9], are 5.97, 5.97, 8.59 and 8.62 eV, respectively. The OEFs of the 207.5 nm and 216.4 nm spectral lines

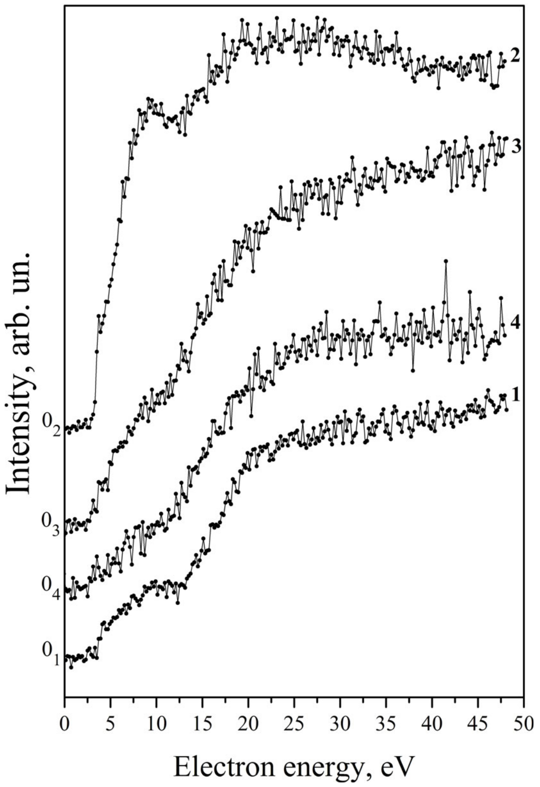

Fig. 3. OEFs for the 360 nm (1), 383 nm (2), 449 nm (3) and 489 nm (4) spectral emissions measured in the electron energy range of 0–50 eV.

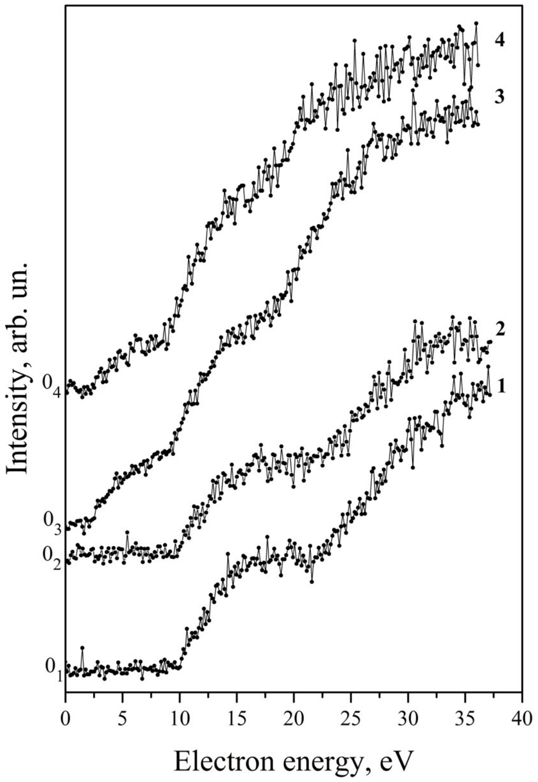

Fig. 4. OEFs for the 207.5 nm (1), 216.4 nm (2), 474 nm (3) and 537 nm (4) spectral lines measured in the electron energy range of 0–40 eV.

are similar since they result from the transitions from the same upper energy level ($4p^3(^4\mathrm{S})5s^5\mathrm{S}^0_2$). The threshold excitation energies of these spectral lines were determined to be 9.6 ± 0.5 eV. The difference between the values for the 207.5 nm and 216.4 nm spectral lines obtained in our work and in [5] is equal to the Se_2 dissociation energy (i.e. 3.1 eV). It is the direct evidence that the particular spectral lines were produced due to the dissociative excitation of Se_2 according to the reaction pathway: $\mathrm{Se}_2 + \mathrm{e} \rightarrow \mathrm{Se}^* + \mathrm{Se} + \mathrm{e}'$ [5]. As for the 474 nm and 537 nm spectral lines, their threshold excitation energies were difficult to be determined because of the intense molecular emission overlap. In the energy range from the threshold (∼3.6 eV) to above 9 eV, these spectral lines reproduce the general character of the molecular emissions' OEFs, the further rise in intensity was caused by the excitation of the final energy levels, i.e. $4p^3(^4\mathrm{S})6p^5\mathrm{P}_{3,2,1}$ and $4p^3(^4\mathrm{S})6p^3\mathrm{P}_{0,2,1}$. A sharp rise can be observed for all the OEFs with a maximum at above 17 eV formed due to the dissociative excitation of Se_2 (17.72 eV) resulting in the excitation of both selenium atoms produced according to the following reaction: $\mathrm{Se}_2 + \mathrm{e} \rightarrow \mathrm{Se}^{*\prime} + \mathrm{Se}^{*\prime} + \mathrm{e}'$ [5].

4 Summary

Slow-electron excitation of selenium in the gas-phase has been studied using an optical spectroscopy method. The emission spectra of the gas-phase selenium have been studied at the incident electron energies of 20, 30 and 50 eV. The optical excitation functions for the molecular emissions as well as the atomic spectral lines have been measured. It has been found that in the selenium vapour the atomic selenium has very low concentration at the 440 K temperature and the main component of the vapour is the Se_2 molecule. It has been demonstrated that the excitation of the atomic selenium occurs due to dissociation of the Se_2 molecule by electron impact.

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