About a strong line shift effect in glow discharges

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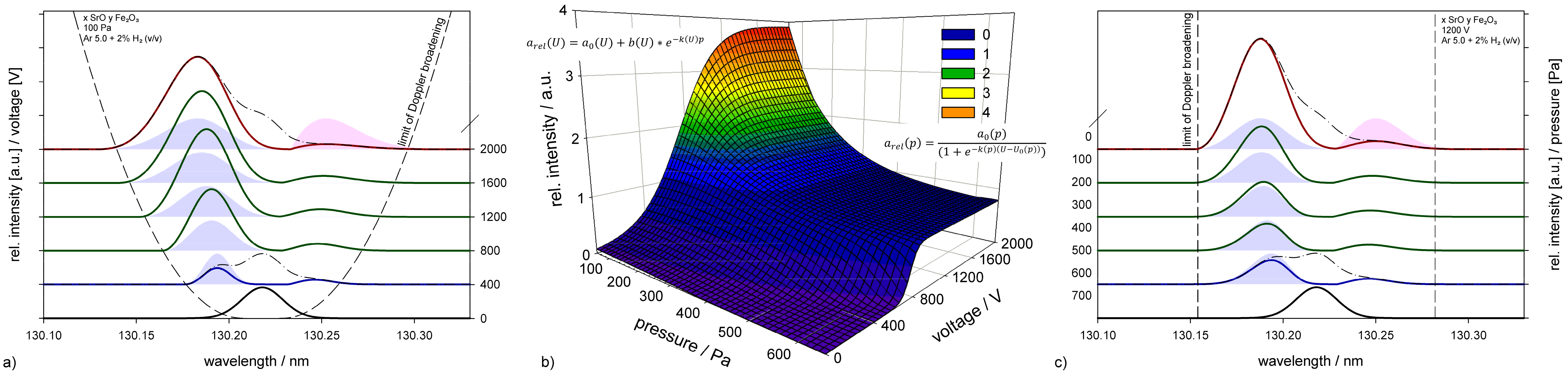

Fig. 1: Fundamental characteristics of the strong line shift effect by the example of strontium ferrite as cathode and argon +2% hydrogen as plasma gas: a) With increasing voltage the intensity maximum shifts slightly towards shorter wavelengths, while the complete peak stays within the Doppler effect [1,2] limit (parabolic curve). b) The ratio of the amplitudes of the blue peak and the initial spectral line depends on pressure and voltage. It changes reciprocally proportional to the pressure. The effect occurs above a limiting voltage U_0. c) A pressure increase leads to a narrower peak. The Doppler effect limit as the predictable extreme of the shift is only reached at the lowest pressures. The spectral intensity distribution was described using the Weibull statistic[3]. Extreme ranges (500 V > U > 1550 V, p > 600 Pa) are calculated by extrapolation.

Abstract

Glow discharge spectra of some oxide materials show a noteworthy blue shift of the oxygen lines. The further investigations presented here, point to the fact, that lines of other electronegative elements from dielectric materials also receive a similar blue shift. Hence, an explanation would be, that these elements represent carriers of the electric charge and leave as negative ions when sputtered. Then, in the cathode fall region, an acceleration would take place in the direction of the optical detector and a correspondent Doppler shift to smaller wavelengths would be the result. The observed blue shift is substantial and under certain circumstances, represents the bigger fraction of a spectral line. Thus, the effect is also relevant in practice.

At the analytic glow discharge spectrometry potential differences from 300 to 1500 V are used. Below some 300 V no sputtering occurs anymore. Just above this level only very low sputter rates are possible. Hence, in daily work electrode voltages between 600 and 1200 V are preferred. Inside the plasma, excitation and ionization take place. Ions are accelerated towards the cathode by the strong electric field. Depending on the different species and the plasma pressure, collision processes counteract. With the end on observation a red shift of the spectral lines of such (positive) ions is to be expected. Because of the vast excitation in the plasma region, in reality only a low fraction of the line intensity is shifted. Up to now the most reported shift effect of glow discharge is a noticeable Doppler broadening of the hydrogen spectrum. At this point red wings as well as blue wings of the spectral lines of the Balmer series[4] appear. The blue shifted fraction is attributed to a reflexion of fast hydrogen atoms at the sample surface. Although for the duties of the analytic glow discharge spectrometry, this special effect appears to be of lower meaning, it is of great use for the understanding of collision processes. The introduced blue shift now shows the general importance of line shifting in glow discharges.

Experimental

In the experiments presented here, a source according to Grimm[5] was used. The construction of such a plasma source is also described in detail in the recent literature[6]. The spectrometer used is a commercial model of the type GDA750 [7] with dc and rf source[8], motor actuated primary slit scanner and additional DK480 monochromator. The monochromator was solely used here for the recording of the Balmer alpha line. The spectral resolution of the Polychromator is 20 pm. The scans were performed at 1 pms^{-1}, respectively 50 pms^{-1} (monochromator).

Influences of material and plasma gas

For the trace levels of oxygen in the gas and use of conductive, inert cathode materials always ideal line shapes are found. The best choice for studying the effect was a non-conductive fast sputtering oxide like strontium ferrite (Fig.1). Conductive oxides show only a relatively weak effect and between dc and rf sputtering there is almost no difference in results. The hematite, which is used here as the conductive sample was not a 100% perfect conductor but includes fractions of silicates and phosphates. An extremely gain of the effect only appears with the atomization of non-conductive oxides. In my experiments this was the only way to produce a small effect also with a neon plasma (Fig.2).

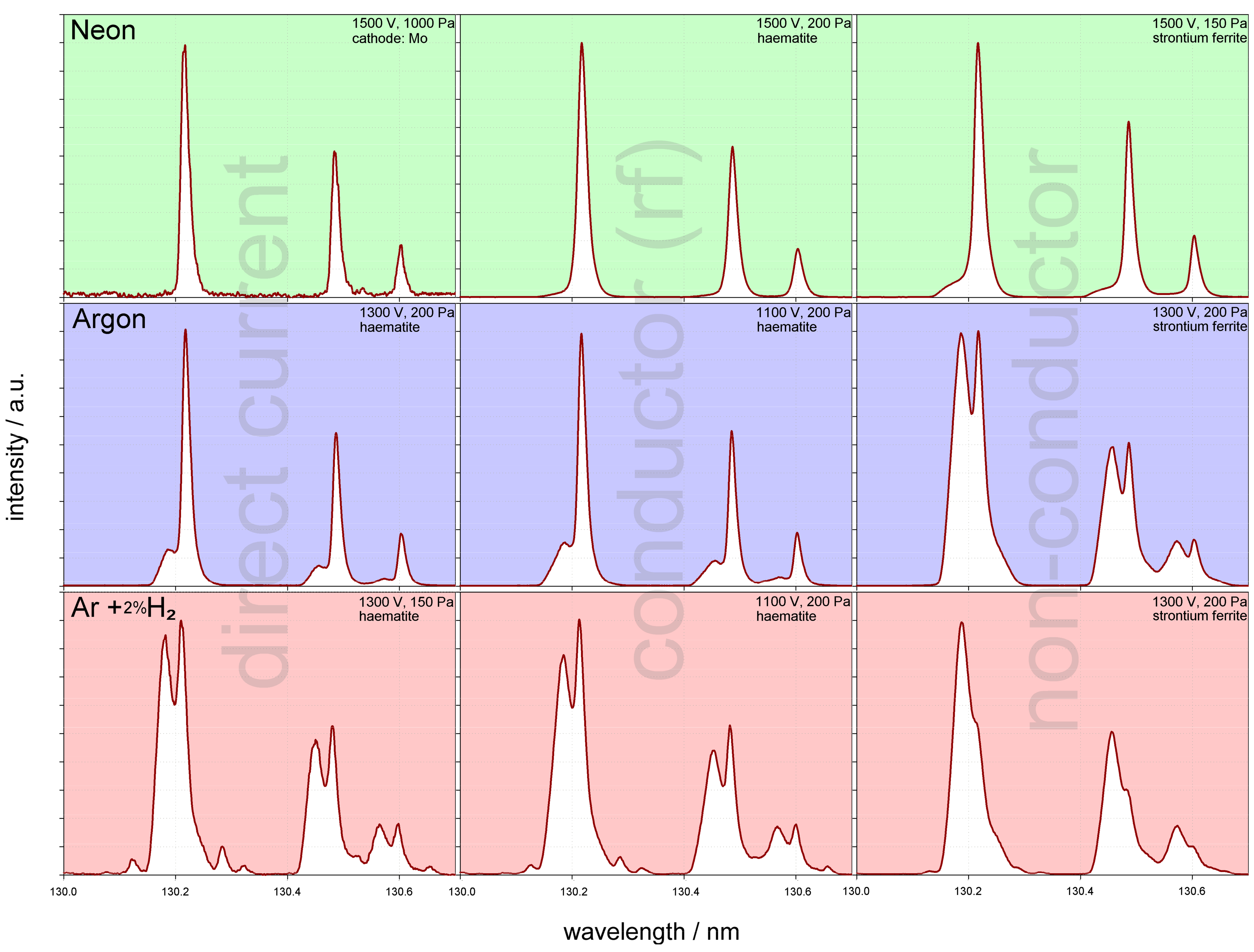

Fig.2: Scans of the oxygen spectral line triplett at 130.217, 130.486 and 130.603 nm [9], with different combinations of gases and materials.

Postulated physical process

To explain the effect one may assume a fundamental influence of a solid dielectric. With conductivity an electron gas exists even in oxides, similar to the pure metallic lattice. It allows a fast electron transport to and from the sample surface. With the sputter process secondary electrons may leave the place of their appearance. This leads to preferential atomization of oxygen atoms which reaches the plasma via diffusion processes.

Since dielectrics must achieve the necessary bias voltage for sputtering, an excess of electrons are accumulated at the surface. The oxygen is bound in the crystal lattice as an ion or may catch an electron when sputtered. Inside the electric field it retains a significant kinetic energy of several 100 eV. The arrival in the plasma region leads to collisions and loss of the electron. The remaining velocity of the oxygen atom is sufficient for the observed blue shift of the spectral lines (Fig.3)*.

*The schematic diagram was made with help of PowderCell[12] and POVray[13].

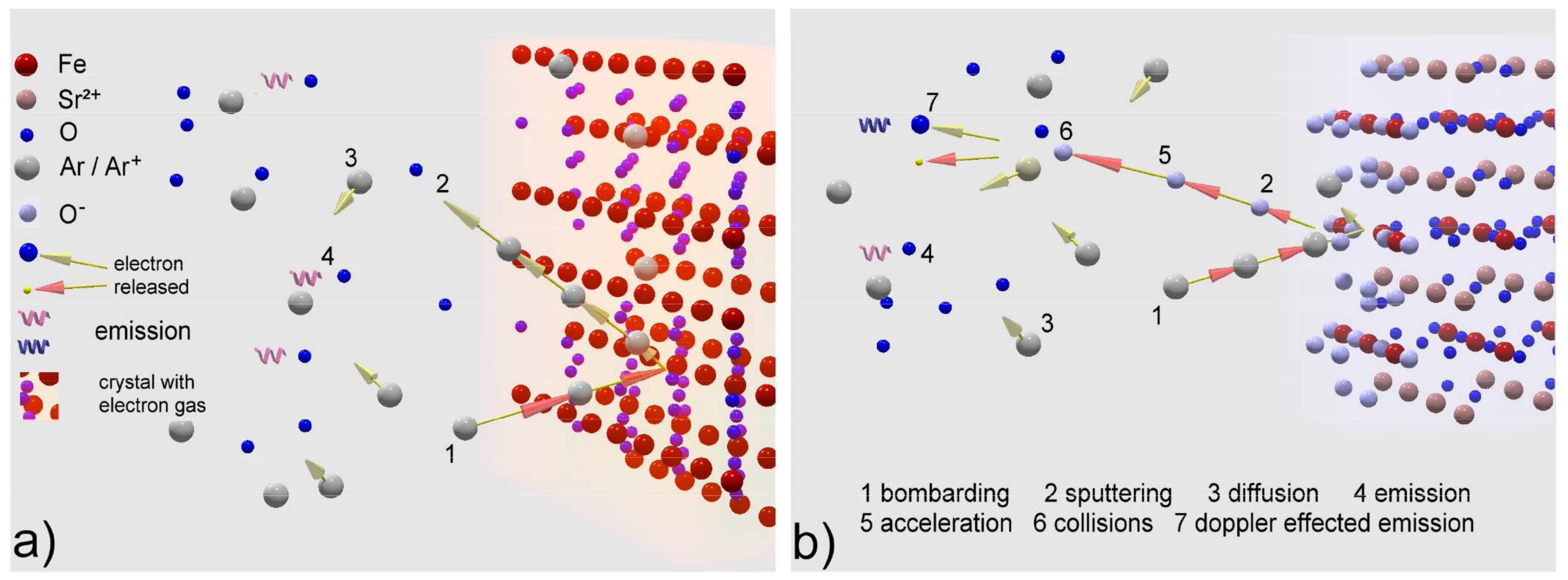

Fig.3: Sputtering and subsequent processes for a) conductive material (hematite[10]) and b) a non-conductor (strontium ferrite[11]).

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Common Doppler effects in glow discharge plasmas

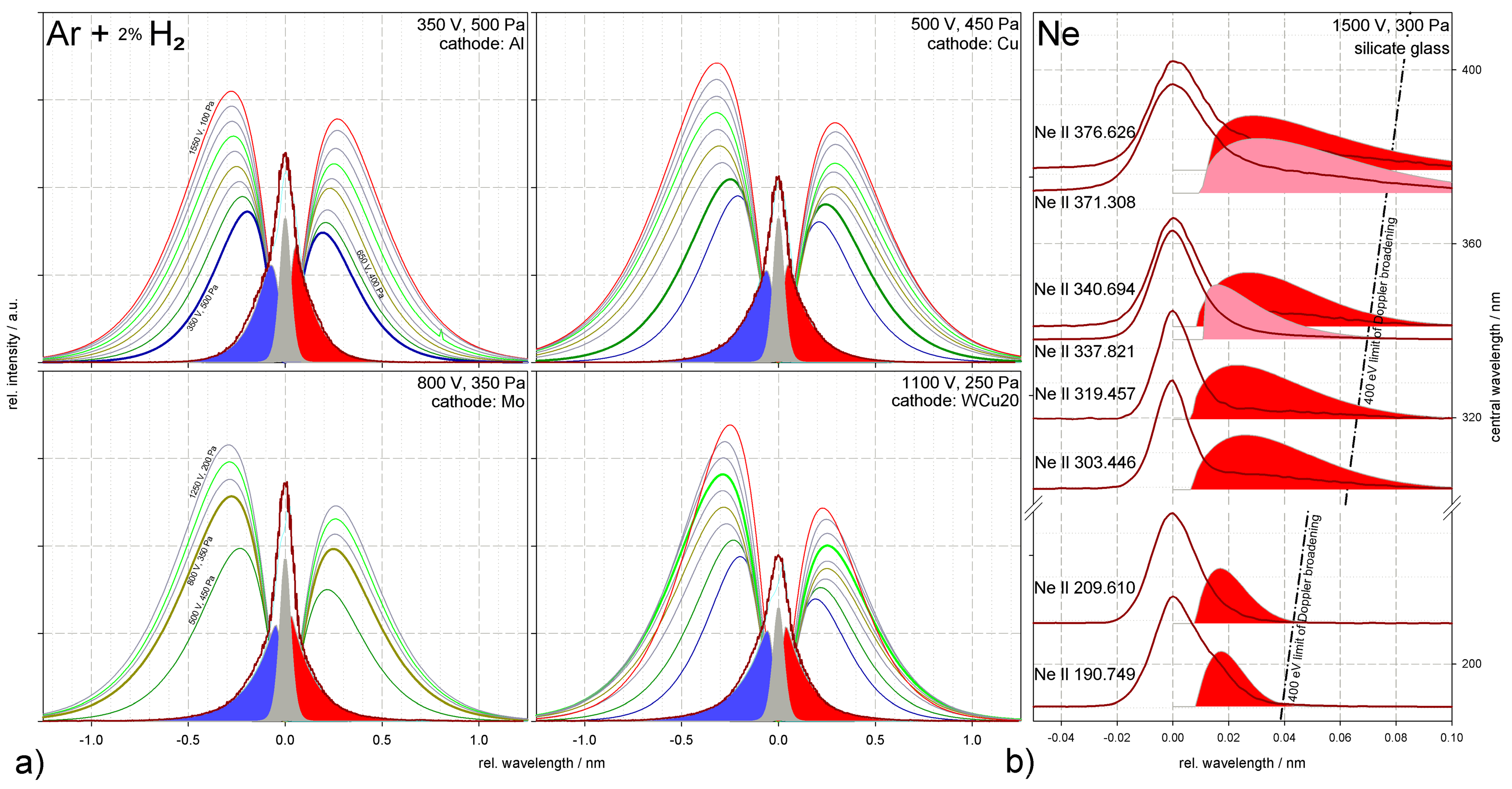

Fig. 4: Appearence of Doppler broadening for a) the hydrogen Balmer alpha line and b) different spectral lines of single ionized neon.

A well-known Doppler effect in glow discharges is the broadening of hydrogen Balmer alpha line. There is a blue and a red wing, both superficially look similar intensive, and have only seemingly little to do with the variation of material or plasma conditions. The intensity of high energetic hydrogen atoms remains only so weak that it can only be noticed with logarithmic representation. However, I´d like to use alternatively the energy content curve [E (Δλ) x I (Δλ)] of the wings (Fig.4). For some additional measurements only such energy curves are included.
With increasing voltage, the line broadens more and more. Also evident is a recently presented material effect on the broadening[14,15]. With increasing density of the cathode material the ratio of blue to red wings intensity grow. This influence is explained with increasing backscatter of hydrogen at the cathode. A "homogeneous" effect can be observed for neon ions. Their spectra show almost exclusively red-shifts. There could be discovered at least two types of shifts. A series of lineshift distributions which appear only for ion energies up to max. 400 eV and other lines which exceed this limit (dashed line). The graph also shows the influence of the radiation frequency on the magnitude of the shift. None of those classical cases show amplitudes and intensity distributions as presented here for the strong "dielectric" shift effect of electronegative elements.

Prospects

Meanwhile, the solely blue shift in solid dielectrics was observed for two more electronegative elements. Again, the broadening could be explained completely with a simple Doppler effect of negatively charged ions. Basically, the use of glow discharge optical emission spectrometry needs certain caution, when non-metallic electronegative elements in dielectric materials or layers are involved or are to be determined. Knowledge and skills are needed for the analytical applications of glow discharge, concerning emission rates of the different species which contribute to the spectrum. It is also necessary to know about those influences on the measurement and to be able to make corrections.

On the other hand, the effect opens a first look on some interesting, new and unexplored* fields of physics. First of all the investigation of events surrounding the atomization of non-conductors by glow discharge sputtering. A use for discovery of certain material properties, such as the nature of the oxide bonds, electrical properties, especially in thin layers, seems to be possible. There would be an application for the effect with depth profiling analyses of thin non-conductive layers, single or multi-phase, or even some bulk materials. Some measurable material-specific parameters of the effect, like the amplitude ratio and the threshold voltage, should be useful for a correlation with certain electrical, mechanical or crystallographic properties.

* Possibly this is not entirely correct. It was just in the last few years, that numerous works to negative ions in plasmas have been published[16-20]. The author so far had no opportunity to study this in depth.

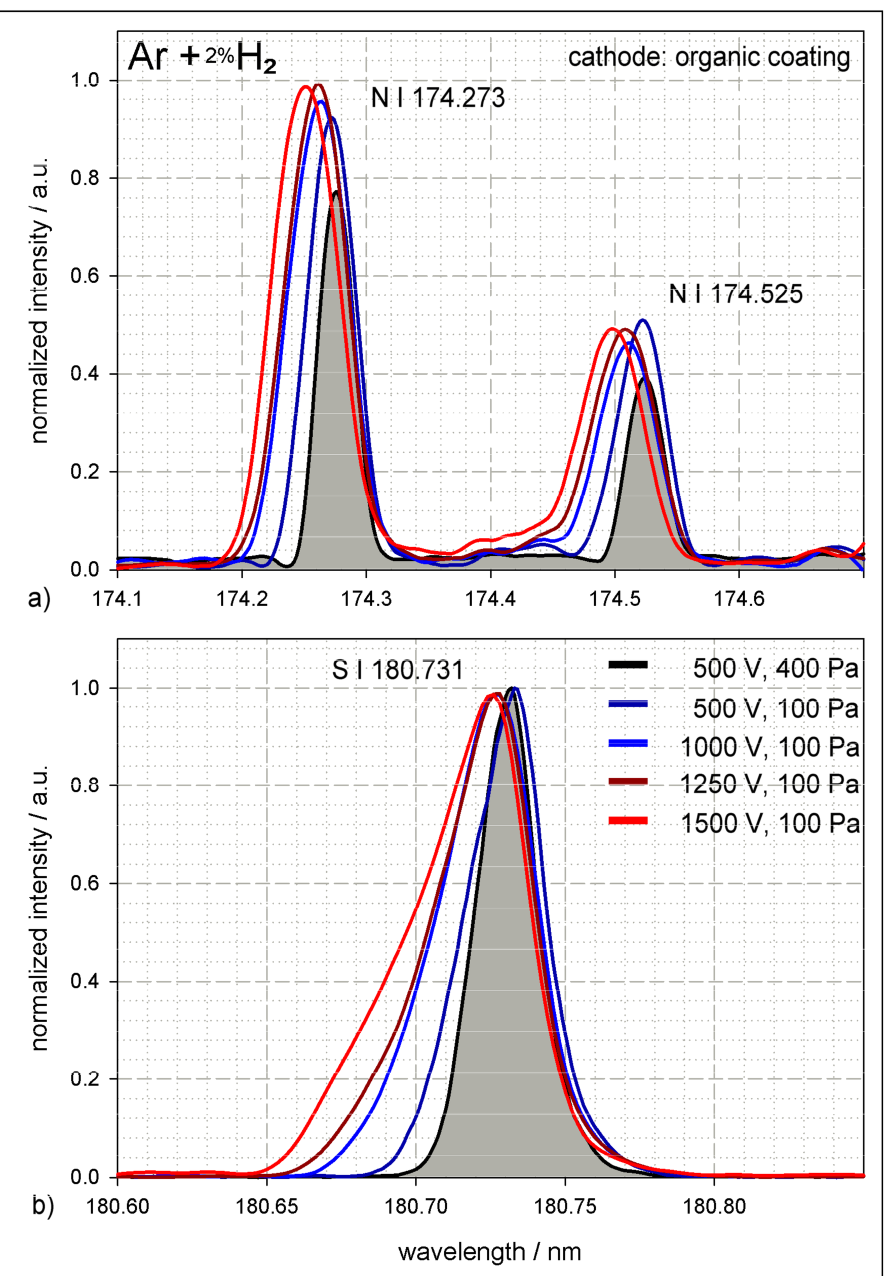

Fig.5: The strong dielectric line shift effect for the nonmetallic elements nitrogen and sulfur: a) line doublet of N I 174.273 nm and N I 174.525 nm with the sputtering of a polymer coating under different conditions. b) The sulfur line S I 180.731 nm during the same measurements. The sulfur is part of the barite addition to the coating.

References

1 Doppler, C. A., “Über das farbige Licht der Doppelsterne und einiger anderer Gestirne des Himmels”, Abh. d. k. böhm. Ges. d. Wiss. , V Bd2, 465-482 (1842).

2 Stark, J., “Über die Spektra des Sauerstoffs (Doppler-Effekt bei Kanalstrahlen)”, Ann. Phys. 26, 806 – 832 (1908).

3 Weibull, W.: „A Statistical Distribution Function of Wide Applicability”, J. of Appl. Mechanics, 293-297 (1951).

4 Balmer, J. J., Ann. PhysikChem. 25, 80 (1885).

5 Grimm, W., „Glimmentladungslampe für spektralanalytische Routinemessungen“, Naturwiss. 54, 586 (1967).

6 Bouchacourt, M., F. Schwoehrer, „Grimm-Source“, Glow Discharge Optical Emission Spectrometry, 54-61 (1997).

7 Analytis, M. , „Spectruma-Analytik GmbH“, Glow Discharge Optical Emission Spectrometry, 143-148 (1997).

8 Wilken, L., V. Hoffmann, K. Wetzig:”Radio frequency glow discharge source with integrated voltage and current probes used for evaluation of discharge parameters”, J. Appl. Phys. 99, 063305 (2006).

9 Moore, C. E., NSRBS-NBS 3, Sect.7 (1975).

10 Blake, R. L., R. E. Hessevick, “Refinement of the Hematite Structure”, The American Mineralogist 51, 123-129 (1966).

11 Grenier, J-C., N. Ea, M. Pouchard and P. Hagenmuller, “Structural transitions at high temperature in $Sr_2Fe_2O_5$”, J. Solid State Chem. 58, 243-252 (1985).

12 Kraus, W., G. Nolze, “PowderCell for Windows Version 2.4”, BAM Federal Institute for Materials Research and Testing, Berlin (2000).

13 POV-Ray for Windows, Version 3.6.2 (2009).

14 Adamov, M.R.G., B. M. Obradović, M. M. Kuraica, N. Konjević : „Doppler spectrometry of hydrogen and deuterium Balmer alpha line in an abnormal glow discharge“, IEEE Trans. Plasma Sci. 31, 444-454 (2003).

15 Steflekova, V. , J. Jovović, N. M. Šišović and N. Konjević. "Balmer alpha line shape and surface morphology during depth profiling analyses of thin film", …*Intern. Symposium on the Physics of Ionized Gases*, Novi Sad, 265-268 (2008).

16 Bentz, B. L., W. W. Harrison: “Negative ions of sputtered cathode species in a glow discharge”, Intern. Journ. Mass Spec. and Ion Phys. 37, 167-176 (1981).

17 Stoffels, E., W. W. Stoffels, V. M. Kroutilina, H. E. Wagner, J. Meichsner: „Near-surface generation of negative ions in low-pressure discharges”, J. Vac. Sci. Technol. A 19, 2109-2115 (2001).

18 Franklin, R. N.:„Electronegative plasmas – why are they so different?”, Plasma Sources Sci. Technol. 11, 31-37 (2002).

19 Katsch, H. M, C. Manthey, J. A. Wagner and H. F. Döbele: “Negative ions in argon-oxygen discharges”, Surf. Coat. Technol. 200, 831-834 (2005).

20 Canulescu, S., J. Whitby, K. Fuhrer, M. Hohl, M. Gonin, T. Horvath, J. Michler: “Potential analytical applications on negative ions from a pulsed radiofrequency glow discharge in argon”, J. Anal. At. Spectrom. 24, 178- 180 (2009).