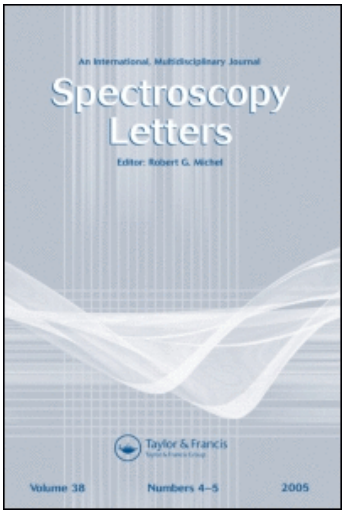

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Laser Optogalvanic Analysis of Nitrogen Layers in Hollow Cathode Glow Discharge

R. Djulgerova[a]; V. Mihailov[a]
[a] Institute of Solid State Physics-BAS, Sofia, Bulgaria

To cite this Article Djulgerova, R. and Mihailov, V.(1993) 'Laser Optogalvanic Analysis of Nitrogen Layers in Hollow Cathode Glow Discharge', Spectroscopy Letters, 26: 2, 347 — 358
To link to this Article: DOI: 10.1080/00387019308011536
URL: http://dx.doi.org/10.1080/00387019308011536

SPECTROSCOPY LETTERS, 26(2), 347-358 (1993)

LASER OPTOGALVANIC ANALYSIS OF NITROGEN LAYERS IN HOLLOW CATHODE GLOW DISCHARGE

Key words: hollow cathode discharge, optogalvanic effect, photoelectric optogalvanic effect, layer and surface analysis

R.Djulgerova, V.Mihailov
Institute of Solid State Physics-BAS
Blvd.Trakia 72, Sofia 1784, Bulgaria

ABSTRACT

This experimental investigation shows that the replacement of the spectral line intensity by the optogalvanic and photoelectric optogalvanic signals improves the accuracy of the classical direct layer-by-layer analysis in a hollow cathode glow discharge and its possibilities, for example for layer thickness measurements in some cases.

INTRODUCTION

The classical hollow cathode glow discharge continues to be applied due to its established qualities as high sensitivity and accuracy of the analyses, effective atom and ion excitation to the high energetic levels, good stability in a wide region of discharge conditions etc[1]. Recently it has been used successfully for a direct layer-by-layer spectral analysis of surf-

aces and metal, semiconductor and dielectric layers[2,3]. In this case it proved to be an ideal source able to sputter the consecutive layers in depth and to give at the same time their analytical signals. On the other hand, the hollow cathode discharge is well known as the most widely used detector for optogalvanic signals[4,5].

The aim of this investigation is the enhancement of the direct layer-by-layer analysis of surfaces and layers in a hollow cathode glow discharge replacing the classical spectral line intensity by the optogalvanic or photoelectric optogalvanic signals of the elements investigated. The last signals are pure electrical signals which is a prerequisite for better analysis characteristics as our preliminary results showed[6].

DESCRIPTION OF THE USED METHODS

The classical direct layer-by-layer analysis is based on the ion cathodic sputtering. The sputtered atoms enter the hollow cathode plasma where they excite and emit their typical spectral lines. Thus, the spectral line intensity I measuring with time t gives very useful information as for example the quality and the quantity of the sputtered atoms, the concentration profiles of the different elements in depth, the mutual diffusion of the different layers, the layer thickness etc[3].

The conventional optogalvanic effect is based on the resonant light absorbance by the plasma of some source that changes the ionization ballance of this plasma resulting in a discharge impedance change. In spite of the difficult optogalvanic signal (OGS) interpretation in most cases the optogalvanic spectroscopy has a lot of applications[4,5]. In this work we combine the advantages of the optogalvanic spectroscopy with

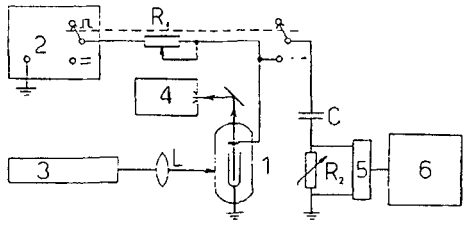

FIG.1 Experimental setup:1-hollow cathode tube,2-power supply,3-laser,4-spectrograph,5-preamplifier,6-selective nanovoltmeter or oscilloscope.

the classical direct layer-by-layer analysis in a hollow cathode discharge.

If a surface placed in a discharge is illuminated by a suitable wavelength light this surface can emit photoelectrons.The discharge can transform these low-energy photoelectrons into high-energy ones having enough kinetic energy for additional ionization, i.e. for producing of optogalvanic effect.Such type of signal named photoelectric optogalvanic signal (POGS) recently has been used for layer and surface analysis in a high frequency discharge[7,8,9].Here we apply the POGS as an analytical signal for layer thickness analysis in a hollow cathode glow discharge.

EXPERIMENTAL

These experiments were carried out on a set-up (Fig.1) consisting of certain standard components: hollow cathode discharge tube with an appropriate design,d.c.or pulse power supply,nitrogen laser , detecting RC-group and an apparatus for analytical signal registration:a spectrograph,an oscilloscope or a selective nanovoltmeter with a preamplifier. The OGS and POGS have an analogous character so they

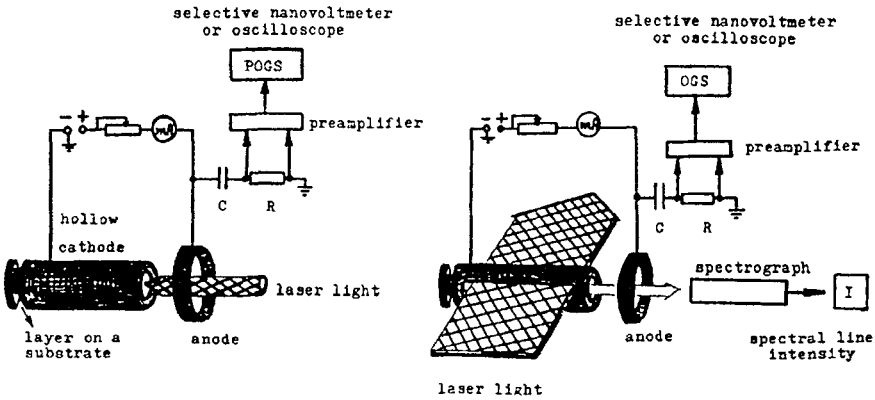

FIG.2 Hollow cathode configurations for photoelectric optogalvanic signal, optogalvanic signal and spectral line intensity measurements.

are detected as the voltage drop change on a resistance R with a suitable value (R=25kΩ÷1MΩ). The condenser C placed before R separated the discharge voltage from the measured one.

Two hollow cathode configurations were developed allowing the different analytical signals (I, OGS and POGS) to be obtained (Fig.2). The POGS arised by illuminating perpendicularly the hollow cathode bottom where the sample was placed. The pure OGS and I were measured by an axial illumination of the hollow cathode plasma through special channels. This way, not only the pure OGS was prevented from the photoelectron background component but also the rectangular cross section ligh emitted by the nitrogen laser could be used in a more natural manner.

The cathode material (Al) and the working gas (He) were chosen to be nonresonant at the 337,1nm nitrogen laser light which ensured the originating of OGS and POGS to be due only to the investigated sample atoms.

The hollow cathode had 6 mm diameter and 40 mm length. The He optimum pressure p was 2,5 torr and the discharge current strength i was 10mA.The laser flux intensity was higher than $10^3 kW/cm^2$.

Taking into account the special ion current radial distribution in a hollow cathode whose density has a maximum at the cathode axis and a decrease toward the cathodic walls,the diameter d of the sample was taken according to the relation $d_{sample}/d_{cathode} < 2/3$ which ensured a plane parallel layer sputtering.

Several Ti nitride layers with different thickness on a Ti-alloy substrates were investigated.These nitrogen layers were obtained by heat-treatment at 900-1100°C temperature in nitrogen atmosphere in order to increase the surface hardness of the material and its resistance to corrosive damages.

RESULTS AND DISCUSSIONS

1.OGS and POGS formation

In order to find out the character of the used OGS and POGS firstly they were registered on an oscilloscope in a pure N_2 discharge at different conditions(Fig.3).The signals are complex having higher amplitude of the negative component.This component is due to the plasma conductivity increase at the laser illumination,i.e.to the discharge current increase which was accepted by us as positive optogalvanic and photoelectric optogalvanic signals.These signals were detected by measuring the increased potential drop on R.The positive component is caused by certain relaxation processes in the illuminated plasma.The POGS=f(i) dependence is proportional to both the negative and positive components while the POGS=f(p) shows an inverse proportionality.In view of the possibility for occurance of various processes in such complex plasma

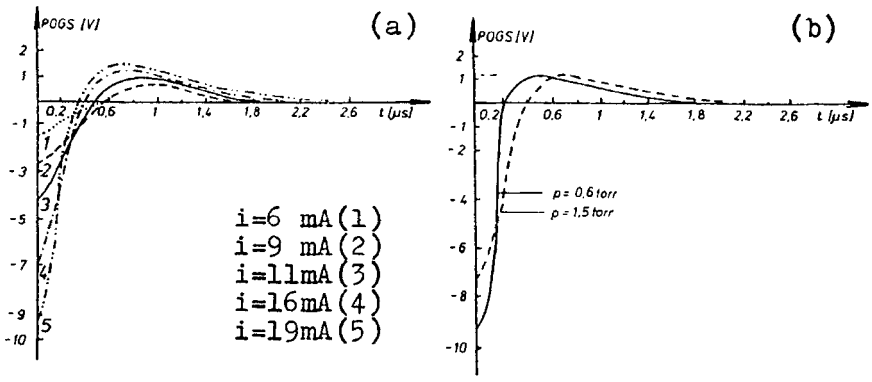

FIG.3 Photoelectric optogalvanic signal shape; POGS=f(i) (a) and POGS=f(p) (b).

consisting of nitrogen atoms and molecules and their ions,He atoms and its ions in some cases,all of them in different ground or excited levels,it is clear that the signal interpretation needs some additional data which will be the object of our next study.Meanwhile, we may use these signals as analytical evidence for the presence of nitrogen in the examined plasma.

We have to note that the meaning of the POGS used by us here is different from those in the works[7,8,9]. In our experiments the POGS were formed not only by the emitted photoelectrons after an acceleration in the discharge but also by a purely optogalvanic effect arising when the sputtered nitrogen absorbed the resonant 337,1 nm nitrogen laser light.That's why in spite of their analogous character the POGS amplitude was higher than the OGS amplitude(Fig.4).The same figure suggests the nonlinearity of the POGS.More detailed examinations carried out by us subsequently have proved the nonlinear character of these signals[10].

2.Nitrogen Layer Thickness Measurement

In order to obtain the nitrogen distribution in

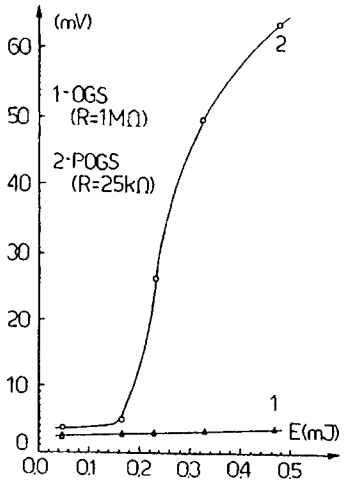

FIG.4 Dependence of the POGS and OGS on the laser light energy E.

depth and the layer/substrate interface position the dependence of the analytical signal (I,OGS and POGS) on time was registered.The layer thickness L of certain samples was measured previously by a metallographic microscope with an accuracy < 1% which allowed us to draw a calibration curve for layer thickness measuring. The detailed microscopical observations showed that there was no good differentiation between the layer and the substrate in most samples because of the nitrogen diffusion deep into the substrate However,the measured microhardness H undoubtedly proved the nitrogen layer existance.For example,the microhardness for the sample with L=72 μm was H=149-177 kg/mm^2 in the basic alloy, H=371-403 kg/mm^2 below the superficial layer and H=508 kg/mm^2 - on the sample surface.

The dependences I=f(t) for some N,N_2,N^+,N_2^+, Ti and Al spectral lines are shown in fig.5 for samples with L=67 μm; 72 μm and 120 μm.The arrow denotes the interface position.The relative standard deviation is 12%.

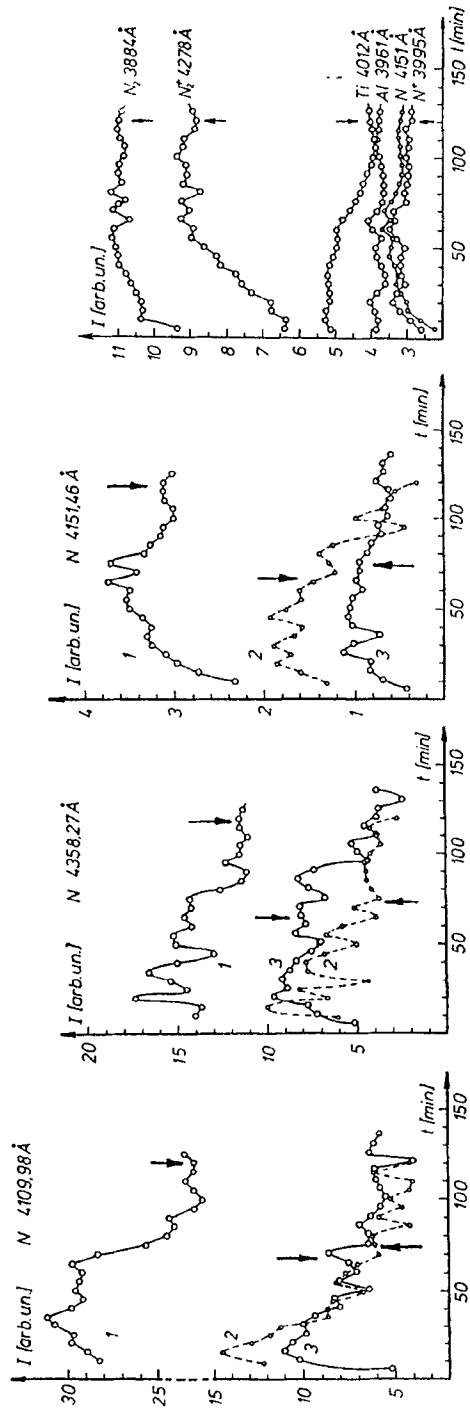

FIG.5 Dependence of the different spectral line intensity on time:L=120μm(1),L=72μm(2),L=67μm(3)

It is not easy to use these dependences for exact interface position determination for the samlpes both with (L=67 μm) and without (L=72;120 μm) exact differentiation between the layer and the substrate since these layers have not too good homogeneity.The tendency of Ti spectral line increasing towards the substrate is logical but the behaviour of the I=f(t) for Al I 396,1nm spectral line of the cathode material is interesting. This function should be expected to be constant but the figure demonstrates its decrease with time.This is caused probably by the nitrogen cover of the cathode surface in the nitrogen atmosphere.In this line we could draw attention to the experimental fact that after a few hours working in nitrogen atmosphere all surfaces of the hollow cathode discharge tube have been covered with nitrogen films.It caused the necessity for their cleaning before the next experiments in order to prevent dscharge instabilities.

The cathode sputtering velocity of the nitrogen layers estimated from figure 5 is 1 μm/min.

The OGS=f(t) dependence for the samle with L=120μm layer was registered simultaneously with the I=f(t) dependence at the same discharge conditions (Fig.6). A clearly expressed minimum corresponding to the interface position is seen in this function so it can be used for the layer thickness measurements.

The POGS=f(t) functions for samples with L=67;72 and 120 μm are shown in fig.7.Here we would note very clearly shaped minimums in these curves corresponding to the previously measured thickness of the layers. Extremely sharp is the minimum for the L=67 μm thickness layer which is very well differentiated from the substrate as the microscopical observation had showed. In regard to these functions after the interface it can be noted a high POGS,even higher than in the

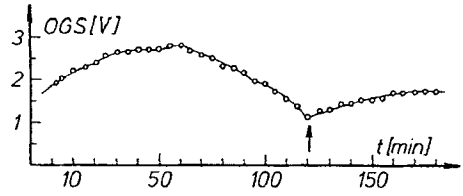

FIG.6 Dependence of the optogalvanic signal on time for L=120 μm sample.

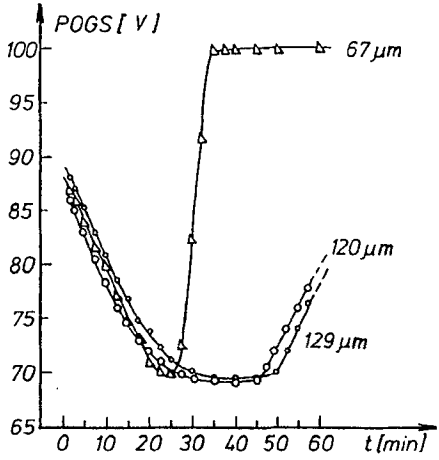

FIG.7 Dependence of the photoelectric optogalvanic signal on time for different thickness layers.

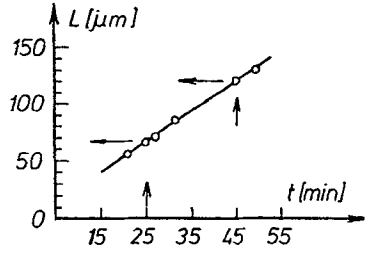

FIG.8 Calibration graph for layer thickness measurement

nitrogen layers,with a tendency of saturation.The explanation of this result could be found in the following considerations.On one hand,the impurities for example the soluble gases in the metal are known to decrease often the work function necessary for photoelectron emission[11].On the other hand,the soluble in the metal nitrogen can enter easily in the hollow cathode plasma giving a high optogalvanic component in the photoelectric optogalvanic signals.

The velocity of cathodic sputtering in the last experiment was estimated to be 2,7 μm/min.It is different from those estimated by the figures 5 and 6 because of the higher discharge current density.

The relative standard deviation becomes 3÷6% using the OGS and POGS.

Due to the POGS very high sensitivity to the interface position the function POGS=f(t) can be used for layer thickness/time calibration curve drawing (Fig.8). This curve can be applied successfully for measurement of nitrogen layer thickness at least of the order of the investigated here.

In conclusion,we could generalize that the classical direct layer-by-layer analysis in some cases can not be reliable and easy for layer thickness measurements as for example when the element investigated consists in both the layer and the substrate and in particular for layers having no good homogeneity.In these cases the replacement of the spectral line intensity by the optogalvanic signal or especially by the optogalvanic pfotoelectric signal as an analytical signal is a good solution due to their much better accuracy and higher sensitivity to the changed interface region characteristics.

ACKNOWLEDGMENT

This work was sponsored by the National Fund for Scientific Investigations.

REFERENCES

1.S.Caroli (Ed.),"Improved hollow cathode lamps for atomic spectroscopy",Ellis Horwood Limited Publishers,England(1985).
2.A.Drobyshev,Jour.Appl.Spectr.(Russ.),56,7(1992).
3.A.Drobyshev,Yu.Turkin,Spectroch.Acta,36B,1153(1981).
4.V.Ochkin,N.Preobrajenski,Usp.phys.nauk(Russ.)148, 473(1986).
5.B.Barbieri,N.Beverini,Rev.Modern Phys.,62,603(1990).
6.R.Djulgerova,V.Mihailov,D.Zechev,Intern.Confer.on Quant.Electr.Techn.Digest Series,9,504(1992).
7.S.Downey,A.Mitchell,R.Gottscho,J.Appl.Phys.63,5280 (1988).
8.G.Selwyn,B.Ai,J.Singh,Appl.Phys.Letters,52,1953(1988)
9.A.Mitchell,G.Scheller,R.Gottscho,D.Graves,Phys.Rev. A,40,5199(1989).
10.R.Djulgerova,V.Mihailov,(to be published).
11.G.Landsberg,"Optics",Nauka,Moscou (1976).

Date Received: 08/21/92
Date Accepted: 09/23/92