# Application of Secondary Electron Emission Spectroscopy for the Investigation of Adsorption Phenomena

PhD Thesis

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## 1. State-of-the-art

Among the numerous types of thermionic electron emitters the dispenser cathodes, the electrodes of high intensity discharge lamps and the arc-welding electrodes are belonging to the group of metal electron emitters – where the electrons escape through an adsorbed layer covered metal surface. The operation mechanism of the above cathodes is based on the formation of a Ba-O double-layer, or a Th or rare-earth monolayer, which are existing in dynamical equilibrium on the top of the cathode surfaces, and are accountable for the diminution of electronic work function. The lighting industry, the CRT (cathode ray tube) manufacturing and the technologies having considerable financial support (such as the military technology and the accelerator physics) put continuous impetus on the cathode research.

Recently in the different fields of cathode research and development there are taken many efforts to increase the electron emission current, to improve the reliability and lifetime of the cathodes and to introduce new, environmentally friendly technologies for example through the replacement of thoria doped tungsten wires. The obtainable maximum emission current is an important aspect of cathode design from the point of view of TV and monitor manufacturing (SAMSUNG, Thomson, LG-Philips), since this is the most evident way to develop the new generation monitors with higher brightness and higher resolution limit. The most important life-limiting processes – including the ion bombardment damage and the cathode poisoning effect – are nowadays a very actively investigated research topics.

The measurement of the electronic work function is a widespread technique to investigate the electron emission characteristics of thermionic (and even field- or secondary emission) cathodes. With the most recent experiments the researchers try to image the work function distribution of solid surfaces with more better and better spatial resolution, and to achieve – if possible – the nanometer scale on work function maps. Many publications are dealing with the local measurement of work function in STM (Scanning Tunneling Microscope) or AFM (Atomic Force Microscope), which serve as a successful tool for observing the electron emission properties of solid surfaces.

## 2. Scope of the study

According to the most recent expectations of science during the doctoral school I was working with an equipment where the local measurement of work function together with the investigation of secondary emission coefficient is available. This method is called *Secondary Electron Emission Spectroscopy* (SEES), which in essence is a useful tool for the analysis of physical processes occurring on electron emitter surfaces.

The work function and the secondary emission coefficient is to be calculated on the basis of the low kinetic energy spectrum of secondary electrons, thus it may be expected, that the shape of the SEE spectrum will be affected by both parameters. For the proper understanding of the SEE spectrum the investigation of the relationship between the work function and secondary electron emission seemed to be essential. I have completed this theoretical explanation on the basis of the Eckart potential barrier model. I successfully expressed the energy distribution of secondaries, while the derived equations account for the relation of surface potential barrier and the change of electron current as well.

I applied the SEES method to analise the electron emission properties of O/W and BaO/W adsorbed systems. I observed both the work function and secondary emission changes induced by different thicknesses of adsorbed layers.

Other series of SEES experiments were performed on contaminated W plates. The main goal of this study was to get reliable results on the emission characteristics of high pressure discharge lamp cathodes by the comparison of well controlled O adsorbed layers and the industrially handled, contaminated W surfaces.

## 3. Experimental

The measurements were performed in the complex surface analytical system of the Budapest University of Technology and Economics Department of Atomic Physics, where XPS (X-ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy) methods are settled. The SEES analysis was carried out by recording the low kinetic energy spectrum of the emitted secondary electrons. In the first quarter of the PhD school I accomplished the required developments and calibration measurements of the tool.

As an electron source a VG Microtech made, LEG 200 type electron gun was applied with 200nm minimum spot diameter, resulting in a minimum spatial resolution of 10μm on the secondary electron images. During XPS the samples were irradiated by a VG Microtech made twin anode x-ray source. Both the MgKα (1253.6eV) and AlKα (1456.6eV) X-ray lines were used to carry out the measurements. For the detection and energy separation of electrons a VG Microtech, CLAM 2 type, truncated hemispherical energy analyser was available having an energy resolution of 0.3eV.

The data collection was obtained by the VGX 900 softver, while I have done the data analysis with the Origin 6.1 and Excel 2003 softvares. The theoretical equations deduced from the Eckart barrier model of secondary electron emission were depicted applying the MATLAB 6.1 program.

The applied and partly developed equipment has in fact the following two main advantages:

- Work function and secondary electron emission measurements and chemical analysis (by XPS method) can be completed *in situ*.
- The spatial distribution of work function and the secondary emission coefficient can be determined by scanning the electron beam. Work function maps and secondary electron images of the same surface area are *in situ* available.

## 4. Summary of scientific results

1. (P5) In case of different thickness adsorbed layers I expressed the relationship of work function and secondary emission using the Eckart potential barrier method. Based on the relevant published data in the literature I deduced an equation for the secondary emission current density of metals as follows:

$$J(E,\vartheta_{Det}) = C \cdot e\sqrt{\frac{2}{m_e}} \cos\vartheta_{Det} \cdot E^{\frac{\kappa-2}{2\kappa}} \cdot E^{-0.89} \cdot \frac{\cosh\left[\chi(\sqrt{E}+\sqrt{E-\Phi})\right] - \cosh\left[\chi(\sqrt{E}-\sqrt{E-\Phi})\right]}{b + \cosh\left[\chi(\sqrt{E}+\sqrt{E-\Phi})\right]}$$

where $\chi = \frac{L}{h} \cdot \sqrt{2m_e}$, and $b = \cosh\left[\frac{\pi}{2} \cdot \left\{\frac{2m_e L^2 B}{\pi^2 h^2} - 1\right\}^{-1}\right]$.

where $e$ is the charge of a free electron, $m_e$ is the mass of a free electron, $C$ is a constant, the $\kappa$ parameter has a value of 0,25 for metals, $\vartheta_{Det}$ is the detection angle of electrons, while the thickness of adsorbed layer is assigned by $L$, the work function by $\Phi$, and the height of the barrier by $B$. By doing so the expression of secondary emission current involves explicitly the physical properties of the adsorbed layers under investigation.

2.a) (P2) I inspected the effect of electron irradiaton on on thin oxide layer covered Si and W samples using $2.5 \cdot 10^{-2}$A/cm$^2$ current density. The primer energy was gradually increased from 150eV to 9000eV. I observed that the secondary emission coefficient decreases as a result of electron beam damage. The change of the emission current has its extremum at around 500-800eV, its value may reach or exceed 16% and 18% for W and Si, respectively. At the same time the increase of work function occurs, its relative change is 9-10% for Si and lower than 0.5% for W.

2.b) (P1,P2,K1) During electron irradiation the amount of secondary electron emission change is in accordance with the total number of secondary electrons escaping the surface. In case of metals and semiconductors the number of secondaries is in fact the highest between 250-1000eV. Taking these results into account I draw the conclusion, that the secondary emission change is caused first of all by secondaries, rather than by primary electrons.

3.) (P3) I have measured the work function and secondary emission of O covered tungsten at the same time under ultra high vacuum conditions. The work function of W increased from 4.55 eV to 5.7eV as a result of 510L $O_2$ gas exposure. I declared that the work function change of this amount induced 200-300% decrease in the secondary emission coefficient of the surface.

4.) (P3,P5) I explained the effect of oxygen doses on the work function and secondary emission of W with the Eckart potential barrier model. By increasing the oxygen coverage the electron energy needed to overcome the barrier will also increase. With well established model calculations I have proven that the secondary electron emission current depends in the first instance on the height of the surface energy barrier. I concluded to an equation of secondary electron current which directly contains the work function of the substrate and the work function change induced by the overlayer. See below:

$$J'(E,\vartheta_{Det}) = C \cdot e\sqrt{\frac{2}{m}}\cos\vartheta_{Det} \cdot E^{\frac{\kappa-2}{2\kappa}} E^{-0,89} \cdot \frac{1}{1+\exp(\gamma \cdot (\Phi_{Szub} + \Delta\Phi_{Adsz} - E))}$$

where $\gamma$ is the slope of the transmission function, $\Phi_{Szub}$ is the work function of the metal substrate and $\Delta\Phi_{Adsz}$ is the adsorbate induced barrier height change. It can be seen, that this equation is applicable for a wide variety of substrate / adsorbate combinations. The calculations are in a fairly good agreement with the experimental results.

5.) (P4,K2,K3) I have shown an experimental evidence that the BaO coated W surface has lower work function and at the same time higher secondary emission coefficient than the elemental or oxide covered tungsten. I measured the work function of clean W to be 4.55eV. However, the work function of BaO coated W – BaO originated from BCT emission material – was found to be 3.8eV, while its secondary emission coefficient was enhanced by 40-50%.

## 5. Publications related to the dissertation

Referred publications


P1.) G. Dobos, Gy. Vida, Z.Toth, K. Josepovits, P. Deak: AES investigation of metal-insulator, **Microscopy and Microanalysis*, 11, 1-5, 2005***

P2.) Gy. Vida, I. Beck, V.K. Josepovits, M. Győr, P. Deák: Electron beam induced secondary emission changes investigated by work function spectroscopy, **Appl. Surf. Sci** Vol 227/1-4 pp 87-93, 2004

P3.) Gy. Vida**,** V.K. Josepovits, M. Győr, P. Deák: Characterization of tungsten surfaces by simultaneous work function and secondary electron emission measurements, **Microscopy and Microanalysis,** 9 (4), 337-342, 2003

P4.) György Vida, Ildikó Beck, Katalin V. Josepovits, Miklós Győr: Application of WFS for simultaneous work function and secondary electron emission measurements, **Mater. Sci. Forum,** Vol.473-474, p.293-297, 2004

P5.) előkészületben
Gy. Vida, G. Dobos, *Interpretation of the secondary electron emission spectra of O/W system applying the Eckart potential barrier model*, **Appl. Surf. Sci.**

Non-referred publications

K1.) G. Dobos, Gy. Vida, Z. Tóth, V.K. Josepovits, P. Deák, *Investigation of inhomogeneus metal-insulator samples,* EMAS 2004, 6$^{th}$ Regional Workshop on Electron Probe Microanalysis of Materials Today, Slovenia, 2004

K2.) Ildikó Beck, György Vida, Katalin V. Josepovits, Miklós Győr, *Research of electron emission properties of tungsten cathodes***,** 4th Hungarian Conference and Exhibition on Materials Science Testing and Informatics, Balatonfüred, Hungary, 22-25. October 2003

K3.) Ildikó Beck, György Vida, *Electron emission properties of tungsten electrodes measured by work function spectroscopy*, Spring conference for Hungarian PhD students, Sopron, Hungary, 19-22. May 2003

## 6. Other publications

Referred publications

E1.) Zs. Makkai, B. Pécz, I. Bársony, Gy. Vida, A. Pongrácz, K.V. Josepovits and P. Deák, *TEM investigation of isolated SiC nanocrystals in* $SiO_2$, **Appl. Phys. Lett.** 86, 253109, 2005

E2.) Zs.J. Horváth, L. Dózsa, O.H. Krafcsik, T. Mohácsy, Gy. Vida**,** *Electrical behavior of Al/$SiO_2$/Si structures with SiC nanocrystals,* **Appl. Surf. Sci,** Vol 234, p 67-71, 2004

E3.) Zs. Makkai, B. Pécz, Gy. Vida, P. Deák, *TEM characterization of epitaxial 3C-SiC grains on Si (100),* **Inst. Phys. Conf. Ser***,* Vol.180, p.265, 2004

E4.) Kovách G., Csorbai H., Radnóczi Gy. Z., Vida Gy., Pászti Z., Pető G. and Karacs A.: *Properties of High-density Amorphous Carbon Films Deposited by Laser Ablation,* **Mater. Sci. Forum**, Vol.414, p.127, 2003

E5.) Olga H. Krafcsik, György Vida, Katalin V. Josepovits, Peter Deák, György Z. Radnóczi, Béla Pécz and István Bársony: *Void-free Epitaxial Growth of Cubic SiC Crystallites during CO Heat Treatment of Oxidized Silicon*, **Mater. Sci. Forum***,* Vol.394, p.359, 2002

E6.) O. Krafcsik, G. Vida, I. Pócsik, V.K. Josepovits, P. Deák
*Carbon diffusion through $SiO_2$ from a hydrogenated amorphous carbon layer and accumulation at the $SiO_2$/Si interface*, **Japanese J. of Appl. Phys**., 40, 2197-2200, 2001

E7.) Csongor Suba, Krisztina Kovács, Gábor Kiss, György Vida, Norbert Velich, Lajos Kovács, Bence Kádár and György Szabó: *Study of the interaction between Ti based osteosynthesis plates and the human organism by XPS, SIMS and AES methods*
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Seminars

EE1.) Gyorgy Vida: *Isolated SiC nanocrystals in* $SiO_2$, Solid State Seminar, Fall season, **The University of California at Berkeley**, College of Engineering, Oct. 14. 2005

Non-referred publications

EK1.) Zs. Makkai, B. Pécz, Gy. Vida, P. Deák, *TEM characterization of epitaxial 3C-SiC grains on Si (100) and Si (111),* **XIII. Microscopy on semiconducting materials, Cambridge**, England, 2003

EK2.) Zs. Makkai, Gy. Vida,, Josepovits KV, Pongracz A, Barsony I, B. Pécz P. Deák, *Electron microscopy of SiC nanocrystals*, **European Microscopy Congress, Antwerpen**, Belgium, 2004, Conf. Proc: Vol. II p.191-192, 2004

EK3.) Vida György**,** Suba Csongor, Pethő László, *Properties of anodic $TiO_2$ covered oral implants as measured by surface analytical methods*, Spring conference for Hungarian PhD students, Sopron, Hungary, 19-22. May 2003

EK4.) Cs. Suba, N. Velich, Gy. Vida, Gy Szabó, *In vitro study of $TiO_2$ coated osteosynthesis implants by XPS and SIMS*, Scientific meeting for PhD students, Semmelweis University, Budapest, Hungary, 10-11. April 2003

EK5.) Kovách G., Csorbai H., Radnóczi Gy. Z., Vida Gy, Pászti Z., Pető G. and Karacs A.

*Properties of laser ablated amorphous carbon layer,* 10$^{th}$ European Conference on Diamond, Diamond-like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide, Porto 2000