

Electron stimulated thorium adatom enrichment on the surface of thoriaated tungsten below 2300 K

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Abstract

The evolution of the surface composition of thoriaated tungsten has been followed up by means of Auger electron spectroscopy (AES) upon various heat treatments performed below 2300 K. It turned out that the surface composition dramatically depends on the current density of the electron beam exciting the Auger electrons, and no Th adatom enrichment has been observed without electron beam irradiation in this temperature range. It has been shown that the sources of Th adatoms are the thoria particles attached to the free surface of the wire. It is proposed that electron irradiation induced oxygen depletion of the W–ThO₂ system is the main reason for thorium release onto the free surface from the thoria particles. The relation of the topic to the electrode performance in metal halide lamps is also discussed.

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1. Introduction

1.1. Electrode performance in metal halide lamps

Since thorium is radioactive, it is desirable to replace classical thoriaated tungsten electrodes with other types of electrodes, whenever it is possible. This motivation also has its own effect on metal halide lamp development. Several papers reported on successful trials in which pure tungsten electrodes were applied instead of thoriaated tungsten electrodes in metal halide lamps of “identical design” [1,2]. One should, however, stress that Varanasi and Brumleve [2] state explicitly a very crucial point of this replacement. The lamps with pure tungsten electrodes were also dosed—in addition to NaI, ScI₃—with ThI₄, and they were also doped either with Sc chips or with SiI₄. Similar successful trials

were presented on the 10th International Symposium on the Science and Technology of Light Sources in Toulouse in 2004 [3–5]. Varanasi and Brumleve [3] claimed that 400 W quartz metal halide lamps of identical design containing NaI, ScI₃, ThI₄ salts, and Sc metal chips had quite similar performance in the first 3000 h of operation, if they were fabricated with the following electrode variants: (a) La₂O₃–Y₂O₃–ZrO₂ doped tungsten, (b) K–Al–Si doped tungsten, (c) CeO₂ doped tungsten and (d) standard thoriaated tungsten. These studies also reported on a marked increase of the recovered ThI₄ concentration with increasing burning times in lamps with thoriaated electrodes [3–5]. These results reached and/or allow the following conclusions:

- (i) The increase of the recovered ThI₄ concentration is a direct piece of evidence for the thoria loss of the thoriaated tungsten electrodes in the course of metal halide lamp operation.

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- (ii) The applications of Sc chips (or of SiI₄) might be considered as a hint, according to which the dosing method of metal halide lamps should also establish suitable (i.e. markedly different) oxygen partial pressures at the active electrode surface and at the quartz envelope.
- (iii) One may suspect that the electron emissivity of the non-thoriated electrodes was also increased by Th adatoms that were adsorbed on the electrode surface via the reactive adsorption of Th containing gas species.
- (iv) Since thorium leaves the electrode in form of various species (like Th atoms, ThO molecules or ThO_xI_z molecules), the Th adatom coverage will also be sensitive on the surface composition and on the convection field of the gas phase, especially if halogen mediated transport reactions are active.
- (v) Since the electron emissivity of the electrode is governed by the adatom composition of its surface, one may suppose that the transport rates of the reaction products in the gas phase will be of importance. Although one may suspect that the high neutral gas pressure in metal halide lamps alone will not be effective enough to sufficiently suppress the desorption flux of the Th containing species from the electrodes. The diffusional transport of the surface reaction products in the gas phase will have its own importance, since the desorption flux may become diffusion limited, when the desorbed species leave the solid surface via gas diffusion through a thin neutral gas layer in which the gas velocity is parallel to the solid surface (“Langmuir layer”). This kind of rate limitation is exploited (and numerically modelled) in gas filled incandescent lamps, where the tungsten evaporation rate is markedly decreased with increasing pressure and molar mass of the neutral fill gas [6].

One may, therefore, conclude that the effective Th adatom coverage on the active electrode surface will be established through the competition among the surface reaction and transport rates of the various species. Transport processes are of primary importance, too. These are: (a) the Th and O transport rates in tungsten and (b) the fluxes of Th and O containing species in the gas phase. (Of course, the co-adsorption of other gas components (e.g. Sc or Na) might also be of importance in these processes.) The final conclusion is: modelling of metal halide lamps rests also on an adequate model for the thoria decomposition in tungsten, as it may markedly affect the effective Th and O transport rates in thoriated tungsten.

The quoted works suggest that the Th loss of the electrode is important even if the gas phase is doped with ThI₄. Therefore, we intended to get an insight into the mechanisms through which Th may be emitted into the gas phase.

The primary aim of the present work was to reveal the nature of thoria dissociation and the various states of binding of produced Th and O atoms at the typical electrode

temperatures of metal halide lamps. In this context let us note that the electrode temperatures obey complicated rules in metal halide lamps: they vary in a cyclic way and depend also on the electrode tip geometry [7]. The typical electrode temperatures in vertical D2 35 watt lamps are as follows. The temperature of the electrode with hemispherical tip amounts to 2600 K at the end of the anode cycle, while it is about 2400 K at the end of the cathode cycle. For structured electrodes the corresponding temperatures amount to 2900 K and 2500 K, respectively.

1.2. *ThO₂ dissociation and Th transport in tungsten*

As far as we know, only Selverian [8] has performed an up-to-date numerical study of the processes that can supply Th atoms to the free surface from the bulk in thoriated tungsten electrodes. For the sake of clarity let us stress that the direct application of this model to the electrodes of metal halide lamps is not possible, because Selverian based his model on the following basic assumptions. Dissolved Th and O atoms are present on the grain boundaries and in the lattice of tungsten before the lamp is put into operation, and metallic thorium inclusions (or thoria particles with a metallic thoria envelope) are attached to the grain boundaries. Under such condition one may assume that the rate limiting process of the thorium supply to the free surface is thorium diffusion along the grain boundaries. In addition, Selverian assumes that the process of Th adatom desorption takes place in ultra high vacuum (UHV). These assumptions are, of course, valid for the analysis of the experimental data used by Selverian, because they were collected on electrodes that were pre-annealed along the classical route discovered by Langmuir [9], and the measurements were carried out under UHV conditions. The merit of Selverian’s model is that it adequately describes the following classical observation [9–11]. When the operation temperature of a Langmuir type thoriated tungsten in *vacuum* is higher than 2200 K, then the diffusion flux to the free surface becomes lower than the desorption flux of Th adatoms within a relatively short period of time, and for this reason the electron emission also decreases rapidly.

Because the details of the route devised by Langmuir for the “activation” of the thoriated cathodes [9] will also enlighten some important aspects of the arc cathode performance, let us give its crucial parameters. The first step of the applied process (called “flashing”) is a heat treatment at high temperatures (e.g. 2800 K) for a short period of time in order to clean the surface and to produce Th atoms in various states of bonding. A part of thorium will be dissolved in the tungsten grain boundaries (a very small part will be dissolved in the tungsten lattice) and the major part of Th forms either (sub)micron sized inclusions of metallic liquid, or forms a liquid envelop around (sub)micron sized thoria particles [12,13], while the Th adatom concentration of the surface is too low to exert measurable changes in the electron emission properties [9–11]. The second processing step

(the so-called “activation”) is a vacuum heat treatment in the range of 2000–2200 K. It allows the accumulation of Th adatoms on the free surface via grain boundary diffusion [12–14].

Let us turn, now, to the electrodes of metal halide lamps. The crucial point is that they usually are not “flashed” before the first ignition and they start their service at temperatures that are much lower than the recommended flashing temperature of the Langmuir type electrodes. The importance of this condition becomes evident, when one considers the results of the phase analysis performed by Burgers, Geiss and van Liempt [12,13] on straight thoriated tungsten wires which were applied as filaments in historical vacuum incandescent lamps prepared with suitable getters. The main results were: no metallic thorium is formed below 2700 K. Therefore, *the Th supply to the free surface losses its metallic thorium reservoir, when the flashing temperature is not high enough.*

These conclusions are supported also by the results of Ishikawa and Tobuse [15]. They followed up the Langmuir-type two-step activation process by means of AES and electron emission measurements in an UHV chamber having a residual pressure of 10^{-9} mbar. They confirmed the main points of the classical studies that applied less direct methods. The results can be summarized as follows. In order to reduce the work function markedly in an operation temperature interval of 1400–1800 K after an “activation” annealing at 2000 K, the “flashing” temperature must be higher than 2500 K. In addition, the importance of residual gases was stressed by the fact that the saturation value of the emission current at 1400 K (after suitable activation) was one order of magnitude lower in the AES chamber than in the classical closed systems, even if a high flashing temperature was applied.

It is important to note that the thorium loss is also remarkable in such cases, in which the highest annealing temperature is below 2700 K, and consequently, no liquid metallic thorium is formed according to the phase analysis of Burgers, Geiss and van Liempt [12,13]. For example, one half of the thoria content is lost in thoriated polycrystalline tungsten wires (having a diameter of 230 μm) upon annealing at 2400 K for 150 h in vacuum incandescent lamps [12]. Since a comparable thorium loss was absent in thoriated single crystalline wires (Pintsch wires) [12], one may conclude that the grain boundaries play a primary role in the bulk thoria loss.

As far as we now, the kinetics of the thoria loss without the formation of liquid thoria (observed in [11] and in [12]) has not been modelled so far. The modelling efforts encounter the following difficulties:

- (i) The oxygen activity of the used vacuum lamps (their $P(\text{O}_2)$ partial pressure) is unknown.
- (ii) The rates of the surface reactions at the thoria/tungsten interface producing dissolved O and Th on the tungsten grain boundaries and in the tungsten lattice are also unknown.

The present work reports on a peculiar form of thoria dissociation. The primary merit of these results is that in these experiments both the thoria and the oxygen adatom concentration has been measured, i.e. the thoria dissociation was observed at a well-defined oxygen activity. Two sorts of experiments will be reported. The first group provides various pieces of evidence that an electron beam stimulated Th adatom enrichment was observed, and it is unambiguously connected with the presence of thoria particles attached to the free surface, and the rate of thorium adatom enrichment decreases markedly with decreasing beam current, while the second group reveals the kinetics of the enrichment at a sufficiently high beam current, also with respect to the O adatom coverage.

2. Experimental

Tungsten wires containing 1 wt% (10 mg/g) ThO_2 (Plansee Werke #WVMT10) were studied. The sample length was 150 mm, the diameter of the wire was 250 μm . The material has been stress relieved at 1773 K in dry hydrogen (having a dew point of -50°C). The pattern of the grain boundary groovings and the distribution of the thoria particles attached to the free surface have been revealed by scanning electron microscopy (Fig. 1).

The surface of the samples was cleaned by means of Ar^+ ion bombardment in the Auger chamber before starting the

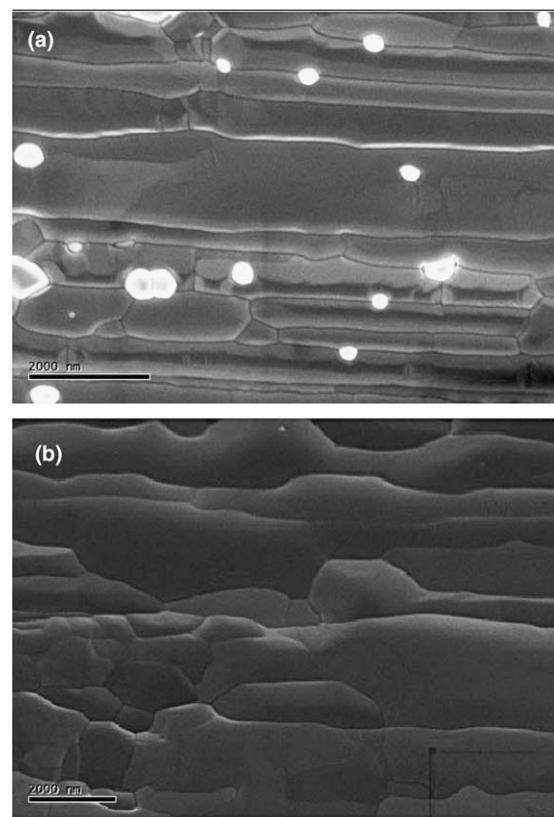


Fig. 1. Scanning electron micrographs of samples: (a) “as mounted” condition and (b) after heat treatment at 2200 K for 27 min.

relevant studies. Thereafter, the sample was heated in the AES chamber by self-resistance heating. The temperature was evaluated by means of the Langmuir tables from the measured hot-to-room temperature resistance ratio of the sample (to this end, potential leads were spot welded to the sample).

The evolution of the surface composition was measured by Auger electron spectroscopy (AES) as a function of the temperature and time. To this end a CMA; PHI-145 type spectrometer was used. The background pressure of the UHV chamber was about 10^{-9} mbar (the oxygen partial pressure was estimated to be lower than 10^{-12} mbar, due to the presence of a solid state getter.). The intensities of the Auger peaks of W (179 eV), O (503 eV), C (272 eV) were recorded as a function of time in differentiated mode at the temperature of the studied heat treatment processes. For Th we have measured the OPV transition of 65 eV, in order to have a good surface sensitivity, since the inelastic mean free path of these electrons is only about 0.62 nm. Surface coverage was calculated on the basis of the AES spectra of pure materials [16]. This calculation might result in a systematic error in the absolute coverage values, but reflects properly the changes due to various effects.

The current density of the exciting electron beam, I_{pri} is given in units of $\mu\text{A}/\text{mm}^2$ (it was measured by a Faraday cap, as usually.). The accelerating voltage of the exciting electron beam varied between 1000 eV and 2500 eV, and the diameter (FWHM) of the beam amounted to 350 μm .

3. Results

3.1. Time evolution of Th as a function of the exciting current

At first, the surface composition of a sample from the “as received” wire samples has been determined in the “as mounted” condition at room temperature. Thereafter, the surface was cleaned by Ar^+ ion bombardment. The resulting surface composition has been tested by means of AES at room temperature. Having received a clean surface, the sample was heated *without* electron bombardment for a period of time at a given temperature (let say 1400 K). Thereafter, the electron gun was turned on with various current densities and primary energies (1 keV and 2.5 keV). Fig. 2 shows a typical result. It is clear that at time zero (when the gun was turned on), there was no Th on the surface. It began to increase and to approach a stationary value merely upon electron irradiation. If the electron beam was shifted to a new position, which has not been exposed to electron irradiation yet, low Th adatom concentration was revealed again that increased upon electron bombardment. The saturation value and the corresponding approaching time strongly depended on the current density (Fig. 2). The time, necessary to reach saturation at a given exciting current, decreases with increasing wire temperature.

Let us stress that we could not find any temperature, where Th appeared on the free surface within a reasonable

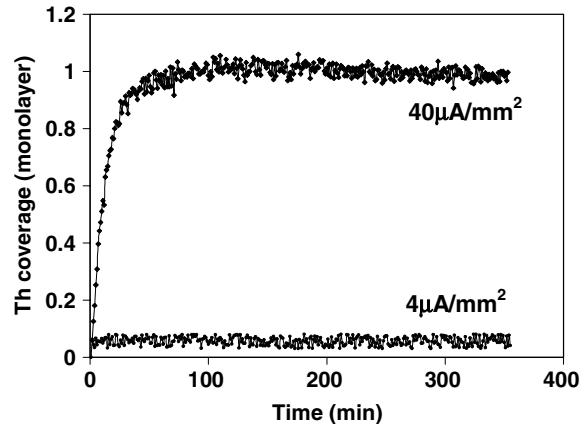


Fig. 2. The evolution of the Th coverage at 1400 K as a function of electron irradiation time applying exciting electron current densities of $40 \mu\text{A}/\text{mm}^2$ and $4 \mu\text{A}/\text{mm}^2$, respectively.

period of time (i.e. within 48 h) without electron irradiation, provided that the sample has never been annealed above 2300 K.

The most direct connection between the electron beam stimulated Th adatom enrichment and the surface attached thoria particles was revealed on samples to which no thoria particles were attached, as a consequence of a longer previous heat treatments performed above 2300 K (see the lower micrograph in Fig. 1). On such kind of samples electron irradiation was not able to produce any detectable Th adatom coverage. When these samples were chemically etched at ambient temperature, a great number of thoria particles were attached to the fresh free surface again, and then the electron beam stimulated Th enrichment reappeared.

3.2. Time evolution of Th at constant exciting current density

According to Section 3.1, the exciting current should exceed a critical value at a given temperature to obtain Th adatoms on the free surface in the studied temperature range. Thus, the voltage and the current density of the exciting current were kept constant at 2.5 keV and $220 \mu\text{A}/\text{mm}^2$, respectively, during all of the experiments reported in this section.

The AES spectra recorded on the “as received” wire were typical of a contaminated tungsten sample; i.e. in addition to the O, C signals only a faint W Auger signal was visible. Although the Ar^+ ion bombardment resulted in a markedly diminished O, and C coverage on the tungsten surface, Th could not be detected in this condition on the surface. In this context, we should emphasize that the sensitivity of the AES analysis is low; the detectability level for Th at the measuring conditions applied is less than 4% of a monolayer. As the area fraction of the thoria particles attached to the free surface is less than 4% (Fig. 1), the ThO_2 particles cannot be detected in our AES analysis.

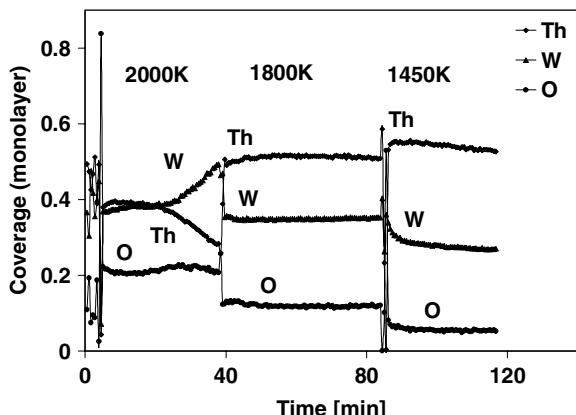


Fig. 3. The evolution of coverage of Th, W and O as a function of time and temperature. Exciting electron current density is $220 \mu\text{A/mm}^2$, beam energy is 2.5 keV.

Thereafter, we performed various heat treatments in the range of 1300–2200 K lasting from some minutes to 24 h. During heat treatments, changes in the Auger signals of C, O Th, and W were continuously recorded. The time evolution of the Th, O, and W Auger signals during a typical experimental procedure is shown in Fig. 3. In this experiment, three consecutive heat treatments were performed at temperatures of 2000 K, 1800 K and 1450 K. Let us note that at 2000 K the Th adatom concentration reached a considerable peak value upon heat treatment, and thereafter the Th coverage decreased markedly with time (the Th adatom decrease might be ascribed either to Th desorption or Th diffusion into the grain boundaries). The crucial point is: the peak value of Th coverage increased with decreasing temperature, and a “quasi-stationary” coverage was maintained at 1800 K and at 1450 K for 40 min. *The evolution of the O adatom signal is also of primary importance: the O signal increased, when the Th signal started to decrease at 2000 K, while the O signal decreased with increasing Th signal at 1800 K and 1450 K.* This kind of behaviour supports the view that the increase of the Th adatom concentration is connected with the oxygen depletion of the free surface.

Repeating the same heat treatment procedure several times, a similar behaviour has been observed: the peak Th coverage increased with decreasing temperature. At any temperatures below 1900 K the Th coverage after a shorter (at higher temperature) or longer time (at lower temperature) approached an apparently “quasi-stationary” value. However, the “quasi stationary” values belonging to a given temperature gradually decreased when the same heat treatment cycles were repeated several times. Ultimately, the Th AES signal has disappeared. This phenomenon is shown in Fig. 4. This figure depicts the “quasi-stationary” values of the Th coverage (in terms of the Th/W signal ratio) collected along the long history of cyclic heat treatments as a function of temperature. (The schedule of the cyclic heat treatment is given in Table 1.) The line and arrow in the figure show the succession of heat treatments.

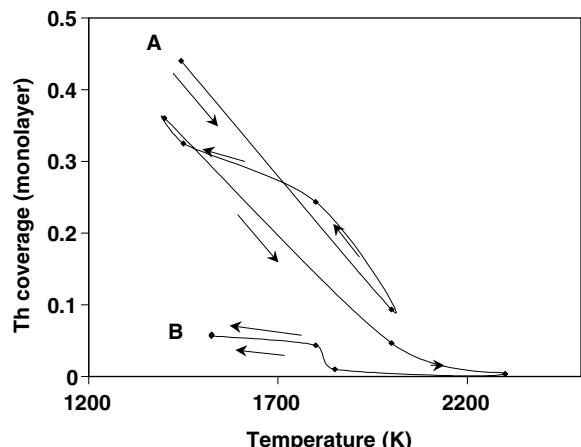


Fig. 4. The changes in the “quasi-stationary” value of the Th adatom coverage obtained upon the cyclic heat treatment schedule given in Table 1.

Table 1

A typical cyclic heat treatment schedule. A and B denote the first and the last heat treatments, respectively

| | Annealing time (min) | Temperature (K) |
|---|----------------------|-----------------|
| A | 214 | 1450 |
| 1 | 39 | 2000 |
| 2 | 48 | 1800 |
| 3 | 31 | 1450 |
| 4 | 86 | 1400 |
| 5 | 29 | 2000 |
| 6 | 27 | 2300 |
| 7 | 54 | 1850 |
| 8 | 96 | 1800 |
| B | 96 | 1525 |

Reaching the last point of the figure with zero Th signal, we could not find any other additional treatment to produce Th AES signal from the free surface of the sample again, provided that temperature of the treatment does not exceed 2200 K. Thus, the source that provided the Th adatoms on the free W surface upon electron bombardment was gradually and irreversibly exhausted upon electron bombardment in the end condition of this sample. Since, in this end condition of the wire no bright spots (that can be identified as thoria particles) were revealed by means of scanning electron microscopy (Fig. 1(b)), while the scanning electron micrographs did show many bright spots in the initial condition (Fig. 1(a)), we may conclude that: *the source of the Th adatoms is the ensemble of thoria particles attached to the free surface.*

4. Discussion

Let us repeat the Langmuir type behaviour of the Th adatom concentration already described in the introduction. When thoriated tungsten is activated by the Langmuir type two-step process under UHV conditions, then the concentration of the Th adatoms is governed by a segregation type process upon the “activation” treatment, in which

thorium atoms diffuse to the free surface along the grain boundaries from metallic thorium inclusions generated during the preceding “flashing” step, provided that the flashing temperature was sufficiently high. Although the thorium transport from the bulk is not able to compensate for the thorium adatom desorption above 2000 K for a longer period of time even after a Langmuir type treatment of thoriated tungsten [8], the “quasi stationary” Th adatom concentration obtained at 2000 K becomes “stationary” at 1800 K for a long period of time (let say for 1000 h), because the desorption rate at 1800 K is sufficiently low for this.

Our observations are in strict contradiction with this Langmuir-type behaviour. The present work revealed Th adatoms on the free surface:

- (i) merely upon electron bombardment with sufficient intensity and energy,
- (ii) the “quasi stationary” coverage at high (but constant) electron current increased with decreasing temperature,
- (iii) no Th adatom coverage was detected after a sufficiently long period of bombardment,
- (iv) good pieces of evidence were presented, that the source of the Th adatoms are the thoria particles attached to the free surface, since the Th coverage of the free surface ceased, when the thoria particles were annihilated through delivering their Th and O content to the free tungsten surface, and through the evaporation of the Th and O containing species from the thoria particles. (of course, Th adatoms are desorbed from the free surface of tungsten with an appreciable rate in our experimental temperature range).

The average coverage of the ThO_2 second phase particles is around 1%. This small amount of (three-dimensional) particles is not visible by AES having a sensitivity of some percentage. Though the surface coverage of the particles is small, the amount of material in these particles is huge, concerning the number of atoms necessary to cover the surface of the wire. Thus, if Th atoms are released to the tungsten surface they might spread from the particles along the surface. In this way they can cover it easily.

Thus, the appearance of the Th adatoms on the tungsten surface is not caused by segregation of the Th atoms dissolved in the bulk to the free surface in the studied temperature range. They were created by the electron stimulated desorption of (various) O containing species, which made the Th release from the ThO_2 particles to the free tungsten surface possible, and then their spreading along the tungsten surface.

We believe that the merits of these finding are as follows. A peculiar kind of dissociation process of thoria has been followed up, in which not only the appearance of the Th adatoms were detected, but also the oxygen coverage of the tungsten surface is measured. This oxygen coverage may be used in a subsequent thermo-chemical

analysis as a quantitative measure of the oxygen activity that allows the dissociation of thoria. In addition, these finding might be considered as a hint that upon the ignition of the arc metal halide lamps such electron induced desorption processes may also play a role in the evolution of the Th adatom coverage in the anode cycle of the electrode.

5. Conclusion

A new type of thorium enrichment on the free surface of thoriated tungsten wires has been observed below 2300 K that lasted as long as ThO_2 particles were present on the free surface. This kind of Th adatom coverage appears merely upon heat treatments performed between 1400 K and 2000 K, if the current density of the electron bombardment on the tungsten surface is sufficiently high. In this case the adatom concentration may reach a “quasi-stationary” value. The reason of the Th adatom spreading seems to be the electron stimulated oxygen depletion of the W– ThO_2 system.

The merit of this work with respect to the performance of thoriated tungsten electrodes need not be the direct application of the electron stimulated ThO_2 dissociation with the parameters at which this process has been revealed in the present study. One may, however, say that the electron and ion stimulated process should also be considered in the ThO_2 dissociation processes at the W/plasma interface in real lamps.

Acknowledgements

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