Galvanoluminescence After The Century

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Abstract. To emphasize the full century of investigation of much known phenomenon observed during electrolytic process in which artificial growth of thin oxide film on aluminum is performed, we still use the almost archaic term galvanominescence (GL). The visible radiation appearance during anodization processes is still not completely resolved because of complex environment and many experimental parameters that dictate the intensity and spectral distribution of GL. In a light of the new interest for thin oxide films on aluminum, especially porous films which are used as nanotemplates for growth of nanostructures such as nanotubes, nanowires, nanocontacts, we decided to renew GL spectral experiments by introducing dynamic ICCD spectral measurements and we tried to fulfill the picture of light phenomena that follow anodic oxidation of aluminum in various electrolytes.

In this article, we give the short review of the most important data on GL in a last century as well as our investigations of GL spectral intensity dependence on anodizing parameters that we have researched in a last few years, with a special focus on existing and possible applications.

SHORT HISTORY OF GL

Appearance of light during the electrolytic process was noticed very long time ago at the end of XIX century by Sluginov[1]. After that, it was investigated and described by Brown[2]. From that time continuous interest for aluminum with wide spread of its applications periodically revive the interest for GL. Thank to very complex mechanism being investigated by many authors several terms was used to name this phenomenon indicating the ascribed mechanism: electroluminescence, chemiluminescence, thermoluminescence etc.

Many theories considering GL phenomena were conducted with more or less success in resolving GL mechanism. Most of the theories are connected to the electron avalanche processes and dielectric breakdown in oxide film. Several authors based their models on the dielectric breakdown models in gaseous conductors (Thowsand discharge).

Zener[3] proposed the quantum-mechanical model of electron-tunneling from valence zone to conduction zone as a source of electrons for dielectric breakdown. Von Hippel proposed the dielectric breakdown model similar to discharge in gases [4], and Fröhlich and Seitz [5] gave detailed investigation of this process.

Later, Forlani and Minnaja[6] investigated the critical field for dielectric breakdown and they calculated the ionization coefficient, but they neglected the screening electric field originating from very slow holes produced during avalanche process. O’Dwier [7] introduced this detail. His theory was used as basic model by several authors. Nevertheless, investigations and theories of the GL were developed sometimes independently from theories of electronic conduction in oxide film.

After its discovery the first study about GL was presented by Berti[8] who concludes that the GL is associated with oxide layer on aluminum. Forrest[9] supposed that GL originate from electron discharge in gases developed during anodization process and this conclusion was reached earlier by Güntherschulze[10].

The most extensive study of GL in Al-electrodes has been made by Van Geel et al.[11]. Van Geel found the GL intensity is proportional to anodization current and is exponentially dependent on anodizing voltage. Furthermore, he discovered that only barrier part of porous film is a source of GL as there is the highest electric field.

Many authors used Van Geel's model and their investigations fulfill great part of period from Van Geel up to day. Among all other Shimizu and Tajima [12] gave maybe the greatest contribution in investigation of GL in both barrier and porous films as well They investigated the GL in many inorganic and organic electrolytes and found that carboxilate ions are sources of GL in organic electrolytes and “flaws” are sources of the GL in inorganic electrolytes. Their model of GL in barrier films is based on O'Dwier's calculation of electric field and density of conduction electrons in aluminum oxide during anodizing process. They also used Van Geels model to explain mutual relation between anodizing parameters and GL intensity.

However, all authors failed to introduce dependence of spectral GL intensity on anodizing conditions. Moreover, an interference effects due to surface pretreatment of the samples were also unrecognized, still perturbating experimental data and leading to wrong explanation of GL curves.

OUR CONTRIBUTION

In a last decade the interest for anodic oxide film was revived again, due to expansion of applications in which arrayed porous alumina, formed in electrolytic process is used as nanotemplate for nanostructures[13, 14]. As we saw a possible application of GL radiation for analysis of growing nanostructures and nanotemplates, we decided to refresh our GL experiments and renew our spectral measurements. Here follows the chronology of our investigation related to GL.

First of our results considering GL are related to the recognition of the GL interference effects[15]. These very strong effects previously mislead the other authors in their interpretations. Discovery of interference effects lead us to development of special GL and photoluminescence (PL) method for determination of film thickness[16, 17, 18] as well as film porosity[19]. Later, we used O'Dwier's calculation procedure and developed more complete GL theory, which includes both avalanching and recombination processes[20]. Theory gave an excellent agreement with experimental results renewing the concept of mean free path for electrons in electron avalanche as well as recombination length.

As a source of GL was still unclear, we focused on spectral measurements of GL radiation and investigation of all parameters affecting it during electrolytic process: type of aluminum, type of electrolyte, preparation, surface etc. In investigating the source of GL, we found almost no data about GL spectra. Actually, only Ganley[21] recorded GL spectra, but not with well-defined experimental conditions. Therefore, we decided to make our own measurements. The problem was that film growth during the anodization is dynamic process and GL intensity changes due to change of many experimental parameters. That is why our first candidate for spectral measurements was porous oxide film. After transition phase during aluminum anodization, parameters of anodization reach the steady state regimen in which GL intensity stays constant sufficiently long for complete spectral measurement. We have obtained GL spectra and researched the influence of anodizing parameters on its shape for the first time[22].

Change in the shape of GL spectrum due to change of anodizing conditions indicates that in the background of GL more than one source of optical radiation could be found. We supposed that uncertainties in a global picture of GL will be resolved during examination of GL in other porous and barrier film forming electrolytes [23, 24] and our results undoubtly pointed to the state of samples governing factor of GL.

Nevertheless, transient regimen in the case of porous films and whole anodization period in the case of barrier films remained unresolved due to change of anodization parameters. To manage this, we made special time-resolved ICCD based detection system , which enables fast spectral measurements during barrier film growth or during transient regiment in porous film. Again, we obtained time-resolved spectra for the first time[25]. The results confirmed a different type of LC in organic and inorganic electrolytes, or a different type of mechanism. Furthermore, during investigation of the pretreatment of aluminum samples on GL spectra, we obtained for the first time well defined spectral lines originating from electron transitions in molecular species developed during anodization process: AlH, AlO, Al_2, AlH_2 [26]. We also found that appearance of these spectral lines is related to the sample pretreatment and to the development of gamma alumina crystalline islands during annealing process. Moreover, the same spectrum is added to the spectrum obtained in steady state regimen in organic electrolytes. Thus, we confirmed existence of more then one source of GL.

CONCLUSION

Our early investigations and discovery of strong influence of interference effects on measured spectral GL intensity resulted in completely new interference methods for determining thickness of the oxide during and after anodization. We have introduced new kind of spectral GL measurements: monochromatic measuring in steady state regimen and time-resolved ICCD based measurements. Our theory of GL in barrier oxide films on aluminum assuming nondestructive electron avalanche as well as recombination process gave an excellent agreement with experiment. In experiments we have resolved two types of GL sources: First-carboxylate anions in inorganic electrolytes and second, molecules-radicals formed during dielectric breakdown processes governed by surface flaws which are recognized in our experiments as crystalline islands of alumina produced in annealing pretreatment . The last mentioned source exposes during anodization in both organic and inorganic electrolytes, so according to surface pretreatment we may have both sources of GL in organic electrolytes.

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