



Effect of heat treatment in vacuum on photoluminescence of anodic alumina

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Introduction

It is known that as porous anodic alumina (PAA) is exposed to UV radiation, the photoluminescence (PL) is observed in the range of 350-650 nm with a maximum at 450-500 nm. At present, it is assumed that the PL of PAA is caused either by a simultaneous action of F^+ -centers and impurities in the form of electrolyte anions embedded in the oxide during the anodizing process¹ or is determined by oxygen vacancies with one (F^+ -center) and two electrons (F^- -center)². In addition, it was shown³ that the PAA PL is due to F^- - and F_2^- -centers in different charge states. In this paper, we consider the possibility of controlling optical characteristics of PAA by modifying the specimens through annealing in vacuum or in air and alloying them with manganese ions.

Materials and Methods

Formation of the PAA was carried out by electrochemical oxidation of aluminum foil (99.99%) in an electrolyte based on oxalic acid (0.3 M). Alloying of the PAA was carried out by adding $KMnO_4$ (0.4 g / l) to the electrolyte. Optical absorption (OA) and photoluminescence (PL) were studied on the original unalloyed specimens and Mn-alloyed PAA specimens annealed at temperatures $T_a = 200, 400$ and 600 °C in air and in vacuum and held at constant temperature for 30 min. The luminescence spectra were measured by using an SDL-2 automated spectrofluorometer. The excitation wavelengths were $\lambda_{ex} = 275$ and 325 nm. The optical absorption spectra in the wavelength range from 200 to 800 nm were obtained using a Cary 500 Scan (Varian) spectrophotometer.

Results and Discussion

A strong dependence of the PL intensity of PAA on the annealing temperature in vacuum was found: at $T_a = 600$ °C, the PL intensity is 15 and 5 times higher than that of the original specimens when excited at $\lambda = 275$ and 325 nm, respectively. As follows from the results obtained, the PL spectra represent broad bands and are qualitatively similar for the original specimens and specimens annealed to 600 °C. As the annealing temperature is increased, an increase in the PL intensity is observed, and for the specimens annealed in vacuum the intensity increase is substantially higher than for those annealed in air. Thus, for the PAA annealed at $T_a = 400$ °C, the intensity rises twofold, and at $T_a = 600$ °C it increases by 4.5 and 1.4 times when PL is excited at wavelengths $\lambda = 275$ and 325 nm, respectively. A different shape of the PL intensity curves is observed for the alloyed specimens. The PL intensity of the Mn ions-alloyed specimens is practically not different from that of the unalloyed PAA specimens at annealing temperatures of 200 °C and 400 °C both in vacuum and in air. A significant difference is observed for the specimens annealed in vacuum at $T_a = 600$ °C. In this case, the PL intensity of the alloyed specimens is much less than that of the unalloyed PAAs and practically coincides with the values found for the samples annealed in air. The increase in the PL intensities is interpreted within the framework of the vacancy mechanism. When annealing in vacuum takes place, a low partial pressure of oxygen is ensured resulting in that the lattice oxygen atoms diffuse into the vacuum (the environment), creating anion vacancies. In case of annealing in air, atmospheric oxygen diffuses into the PAA structure and partially reduces the concentration of oxygen vacancies. This is manifested in smaller values of the PL intensity as compared with the specimens annealed in vacuum. In addition, the conditions for removing hydroxyl groups from the volume of PAA in vacuum and in air may also be different, which determines the difference in the vacancy concentrations. In the alloyed specimens annealed at $T_a = 600$ °C, formation of aggregate centers with the participation of Mn ions is possible, the process of formation of single vacancies being limited. This explains the smaller value of the PL.

Conclusion

It has been found that under annealing of the PAA in vacuum a significant increase in the PL intensity is observed in comparison with the annealing in air. The peculiarity of the PL from the alloyed specimens is that its intensity is lower during heat treatment in vacuum and in air. Based on the assumption that the optical characteristics of the PAA are determined by the F^- - and F_2^- - centers in different charge states, the possibility is demonstrated of changing the PL intensity by modifying the specimens using thermal annealing in vacuum and at high temperatures and by alloying them with Mn ions.

Bibliography

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