

Electrodeposition of GaAs thin films from alkaline aqueous solution

C. GHEORGHIES^a, L. GHEORGHIES^b, G. FETECU^c

"Dunarea de Jos" University Domneasca str., no. 47, 800008 Galati, Romania

^aDepartment of Physics, ^bDepartment of Materials Science, ^cDepartment of Electrotechnique, Galati, Romania

Gallium arsenide thin films were prepared from alkaline aqueous solution. Taking in account other conventional methods of preparing gallium arsenide films, electrodeposition technique has some advantages consisting into small operating and equipment costs, relatively easy control of film properties, and no toxic volatile raw materials. The obtained electrodeposited films from alkaline electrolyte are thick, porous and powdery. Some operation parameters namely: electrolyte composition and its pH, applied potential, current density, cathode material, temperature have an important influence on the electrodeposition process. X-ray diffraction patterns of gallium arsenide thin films show a crystalline phase after annealing process. Energy dispersive spectroscopy showed that the deposited films contain different amounts of gallium and arsenic that are in relationship with certain operating parameters.

(Received May 30, 2007; accepted August 22, 2007)

Keywords: Gallium arsenide films, Alkaline solution, Electrocoating, Structure

1. Introduction

Gallium arsenide is a semiconductor material having many desirable properties: it has an ideal direct band gap of 1.43 eV, is highly absorptive and relatively insensitive to heat, it can be allowed with many materials and it is radiation resistant [1]. Gallium arsenide is used as semiconductor laser material and the high frequency transistor as well as the outer space solar cells because it is radiation resistant. The mobility and the saturation velocity of the electron are fast.

There are many techniques of preparation of compound semiconductors such as rf-sputtering, vacuum deposition, vapor phase deposition, chemical vapor deposition, and electrodeposition. Electrodeposition is fast becoming the method of choice for producing films and nanostructures of metals, semiconductors, and metal oxides. In electrodeposition, solid films are deposited at the electrode surface from molecular and ionic precursors in solution. The morphology and orientation of electrodeposited films can be precisely tailored by controlling the pH, applied potential and solution additives. The advantages of the electrodeposition process are as follows: (a) the preparation of thin film required the composition and the thickness possible by controlling of the composition in the bath, the deposition potential and the total quantity of electricity; (b) the preparation at lower temperature; (c) electrodeposition is a simple process and is available on large scale; (d) electrodeposition makes the doping of the impurity easy. In [2] is reported the preparation of GaAs from GaCl and KCl melt, but in [3] is mentioned that gallium arsenide film is obtained at room temperature by using chloroaluminate melts. In paper [4] is revealed the possibility to prepare GaAs from a melt of

GaCl₃ with 1-methyl-3-ethylimidazolium chloride and AsCl₃ solute. In work [5] is shown that can be prepared of GaAs at 720-760 °C from a molten salt consisting from a mixture that contains Ga₂O₃, B₂O₃, NaF and NaAsO₂. Beach and co-workers showed that by chemical vapour deposition method can be obtained GaAs after the annealing in arsenic of electrodeposited Ga metal into holes of silicon [6]. In [7] and [8] documented studies are dedicated to the preparation of GaAs by electrochemical method in various techniques. Based on thermodynamic calculations and some experiments in aqueous solution, Perrault [9] has shown that GaAs couldn't be electrosynthesized from a simple aqueous solution. Considering the potential-pH equilibrium diagrams for Ga-water and As-water systems, Hower and co-workers [10] reported that it is possible to prepare GaAs by electrodeposition method. It was shown that both the gallium and arsenic could be electrodeposited by using electrolytes having high or low pH. If gallium and arsenic are codeposited, the mixture is expected to be thermodynamically unstable due to the negative free-energy of formation of GaAs. According to the phase diagram of gallium-arsenic, a mixture of Ga and As is not thermodynamically stable and should convert to gallium arsenide with excess gallium or arsenide. Due to thermodynamic stability of gallium arsenide film and advantages of electrodeposition method, in some papers was demonstrated that is possible to prepare GaAs thin films from acid solution [8, 11]. Despite difficulties above mentioned, by a punctilious preparation of solution used for electrodeposition, in this paper is showed that thin films of GaAs can be obtained, fact that was certified by XRD analysis.

2. Experimental

In Fig. 1, is shown a sketch of a typical experimental setup. The electrolytic cell that was used in order to prepare GaAs thin films had a cylindrical symmetry. It contained an electrolyte, a cathode, an anode, a thermometer and a pH-meter probe. The cathodic depositions were carried out on a 5 mm-diameter cylindrical graphite support. The anode was made from a spiral of platinum wire having 20 mm diameter and a pitch of 2 mm. Gallium oxides and hydroxides have minimum solubility at a pH value about of 8. By adjustment of pH can be prepared solution having an acid, pH $\sim$ 3, or basic, pH $\sim$ 13, character. The electrolyte consists from Ga_2O_3 solution where was added As_2O_3 and the pH of electrolyte solution was adjusted by means of concentrated KOH solution.

The deposits from solutions containing arsenic and gallium became black or dark brown, with fine dark brown particles near the cathode which also release numerous bubbles. Higher concentrations of arsenic in the deposit always made the deposit darker. Generally, the deposits from electrolytes containing gallium and arsenic did not have adhesion and are in powder form. During the deposition, the current density decreased in the first minutes, and then increased, probably due to increasing surface area. Part of the deposit could be removed by water rinsing. The brown suspension occurring near the cathode corresponds to arsenic. This suspension changed the solution from colorless to brown, and dissolved in the solution after 1 to 2 h standing, depending on electrodeposition time. The deposit also dissolved in the electrolyte, and the gallium in the deposit disappeared much quicker than the arsenic.

During the electrocoating process, it is possible to develop the evolution of small quantities of heat that lead to the development of some temperature gradients. These can change both the degree of solvation and the pH of the solution. The electrodeposition process can be considered to develop in four stages: impregnation, diffusion, adsorption and chemical reaction. The last two stages can be distinct or not, depending on their kinetics. After electrochemical deposition, some of the samples were annealed in nitrogen atmosphere at high temperature furnace.

A power supply, model MIM, supplied the necessary electrical energy and the cell voltage could be coarse and fine adjusted up to 600 V d.c. By means of a rheostat the current in electrolytic bath was constantly manual keep in a certain range for a selected cell voltage. The cell voltage and the current in electrolytic bath have been monitored with MAVO20 instruments. The pH solution was controlled by means of a SEIBOLO pH meter. The immersing depth of graphite bar in electrolytic bath was of 60 mm.

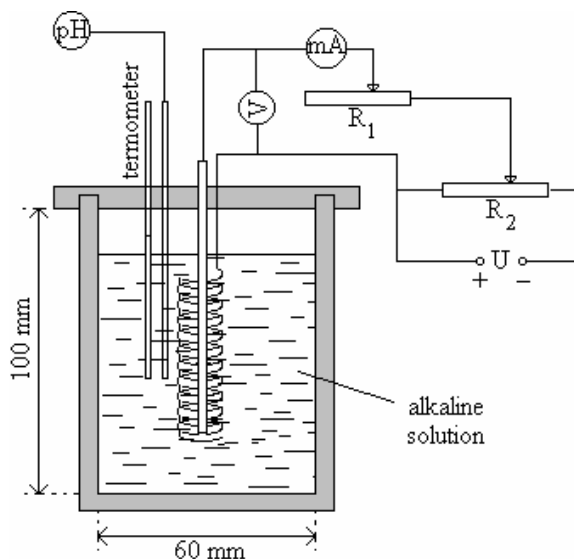


Fig. 1. Schema of the experimental set-up.

3. Structural characterisation

The topography and the thickness of the coatings were relieved by means of interferometric scanning microscope, namely NV 200. In Fig. 2 microscopic images of gallium arsenide electrodeposition as well as some micro-geometric characteristics are displayed.

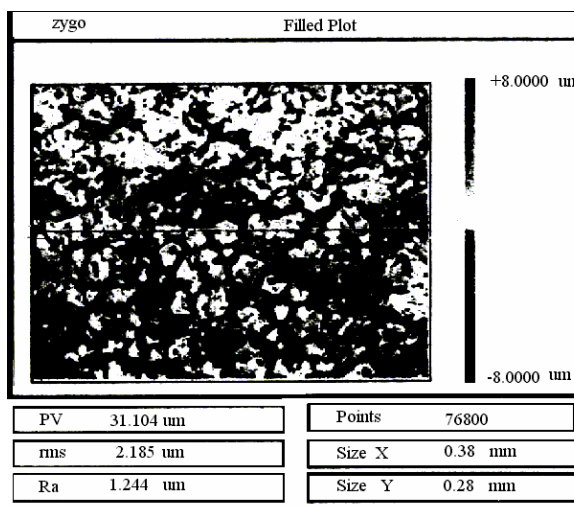


Fig. 2. Microscopic image of GaAs electrodeposition.

In Fig. 3 a surface profile of electrodeposition along the horizontal measuring line that can be seen in Fig. 2.

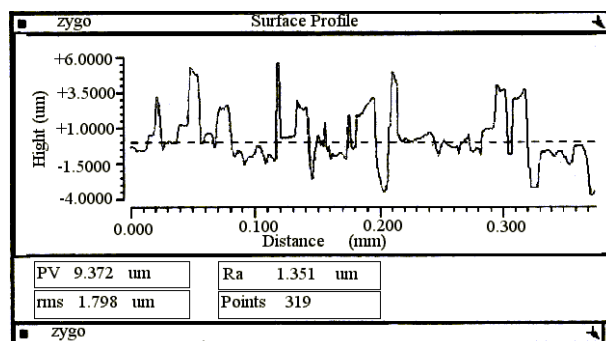


Fig. 3. Surface profile along the analysis line.

The Abbott-Firestone curve, called sometimes the bearing ratio curve, is one of the most important characteristic of a surface because it gives information about the roughness and other parameters referring to the irregularities of the profile. In Fig. 4 the main elements concerning interpretation of Abbott-Firestone curve are presented. A digital device for micro geometry or roughness measurements automatically plots bearing ratio curve, such as presented in Fig. 5. The Abbott-Firestone curve has four intervals, delimited on abscissa axis by ranges $\leq 5\%$, 5-20%, 20-95% and $\geq 95\%$, used for characterizing the functional surfaces. It gives information about the material and void volumes characterising the surface topography and more recently it could be useful for defining and using functional parameters in 3D analysis [12, 13].

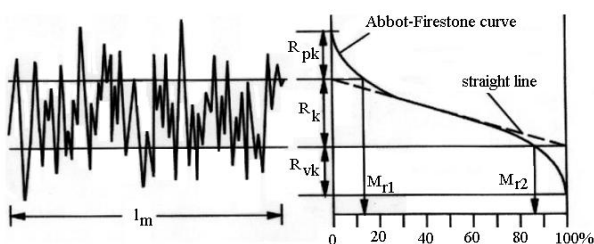


Fig. 4. Main elements of Abbott-Firestone curve.

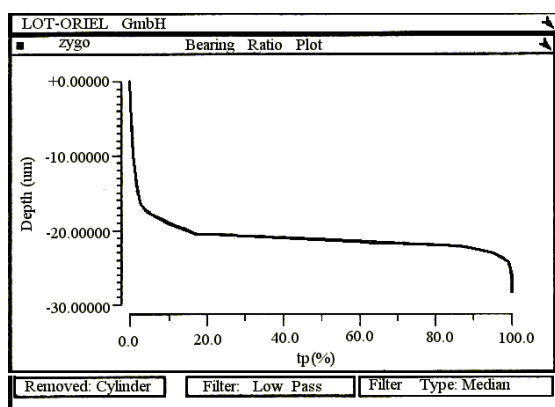


Fig. 5. The Abbott-Firestone curve along analysis line on microscopic image.

The phase analyses have been performed by X-ray diffraction method. To this aim, a diffractometer model DRON 3 having the following operation parameters: $U = 38\text{ kV}$, $I = 30\text{ mA}$, and X-ray tube provided with Cu target and a monochromator in X-ray diffracted beam, has been used. Quanta 200 dispersive spectrometer (EDAX) equipment was utilized for compositional analysis of electrodeposits.

During electrodeposition process near the cathode a lot of bubbles appeared and their formation explains why electrodeposition has a small adherence to substratum. In the electrodeposition process, the current density decreases after a short time and this is probably due to increasing surface area. A brown colloidal gel near the cathode has been observed and the analysis pointed out that it is arsenic. The composition of the electrodeposition is strongly influenced of the applied potential to cathode. Thus, for a solution containing 0.12M Ga and 0.02M As with a $\text{pH}=12.5$, when the potential of cathode increases there is a development of the gallium content in deposit according to a nonlinear law. The temperature of solution plays an important role also on the gallium content in deposit, for a constant electrode potential. The gallium content strongly decreases when the temperature of solution is high. A small temperature leads to a uniform composition in deposit with depth.

In Fig. 6 is shown the dependence of the gallium content in the removed powder sample on electrolyte temperature when the composition of solution is 0.19M Ga and 0.05M As at $\text{pH}=12.5$.

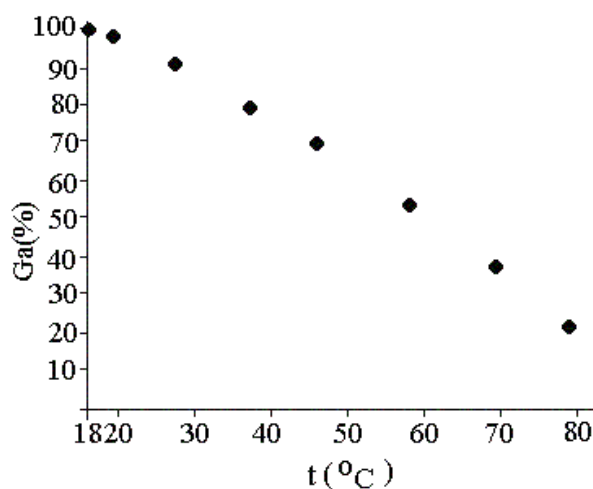


Fig. 6. Dependence of gallium content in GaAs electrodeposit on solution temperature

Generally, the thin films prepared by different methods are in amorphous or in microcrystalline state and become partially or fully crystalline after thermal treatment. In Fig. 7, the X-ray diffraction patterns of the electrodeposits before and after annealing in N_2 atmosphere at 280°C for 15 h are shown.

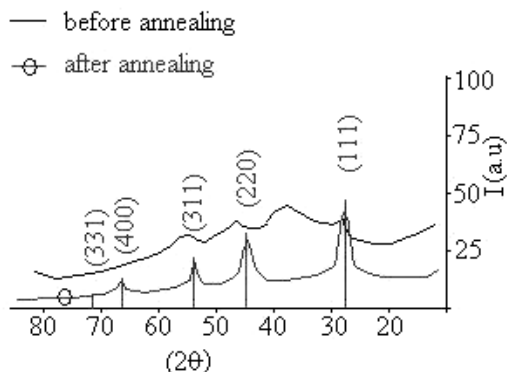


Fig. 7. X-ray diffraction patterns of GaAs films, before and after annealing.

Before annealing the X-ray diffraction spectrum presents some humps that are associated to some microcrystalline formations present into electrodeposited films. After annealing the X-ray diffraction pattern reveals certain structural peaks that are characteristics of crystalline gallium arsenide. Before thermal treatment is found that the gallium contents is smaller comparatively with one after annealing. This fact can be explained taking in account the volatility of arsenic and therefore a growth of gallium content is expected. Despite of difference in amount of gallium and arsenic in electrodeposition before annealing, after thermal treatment in films didn't displayed structural peaks typically to one of the components. Using the Scherrer equation [10] the average dimension of the GaAs mosaic blocks in electrodeposited films after thermal treatment in $\langle 111 \rangle$ crystalline direction and is around 400 Å.

4. Conclusions

Gallium arsenide films were prepared by electrodeposition process from alkaline aqueous solutions. The deposit is thick and pulverulent having relatively poor adhesion to the cathode.

The applied potential, temperature, electrolyte composition and pH can control the composition of the electrodeposition. X-ray diffraction patterns showed that deposited films on graphite cathodes consist from microcrystallites of GaAs.

After annealing in nitrogen atmosphere at 280 °C during 15 h, the electrodeposit exhibits GaAs crystallites with average size of 400 Å in $\langle 111 \rangle$ crystalline direction.

Acknowledgements

Authors express their thanks to Arno Köller from Zigo Company, Darmstadt, Germany, for analysis of electrodeposits at NV 200 microscope.

References

- [1] M. Ruzinsky, V. Saly, E. Aperathitis, Z. Hatzopoulos, *Acta Physica Slovaca* **51**(1), (2001).
- [2] I. G. Dioum, J. Vedel, B. Tremillon, *J. Electroanal. Chem.* **139**, 329 (1982).
- [3] S. P. Wicelinski, R. J. Gale, *The Electrochem. Soc.* **87**, 23 (1987).
- [4] M. K. Carpenter, M. W., *The Electrochemical Society* **89**, 20 (1989).
- [5] R. C. DeMatei, D. Elwel R. S. Feigelson, *J. Crystal Growth*, **43**, 643 (1978).
- [6] J. D. Beach, C. Veauvy, R. Caputo, R. T. Collins, *Appl. Phys. Lett.* **84**, 26 (2004).
- [7] K. R. Murali et al., *J. Mat. Sci.* **2**, 3 (1991).
- [8] M. C. Yang, U. Landau, J. C. Angus, *J. Electrochem. Soc.* **39**, 12 (1992).
- [9] G. G. Perrault, *J. Electrochem. Soc.* **136**, 2845 (1989).
- [10] S. Chandra, N. Khare, H. M. Upadhyaya, *Bull. Mater. Sci.* **10**, 323 (1988).
- [11] C. Gheorghies, L. Gheorghies, *J. Optoelectron. Adv. Mater.* **4**, 12 (2002).
- [12] C. Gheorghies, L. Gheorghies S. Condurache-Bota, Proc. of "The Coating" Conference, Erlangen, Germany, April 5-7 (2004).
- [13] W. P. Dong, P. Sullivan, K. Stout, *Wear* **178**, 1-2 (1994).

*Corresponding author: cgheorg@ugal.ro