Raman study of luminescent spark processed porous GaAs

M. Rojas-López, J. M. Gracia-Jiménez, M. A. Vidal, and H. Navarro-Contrerasa) Instituto de Investigación en Comunicación Optica (IICO), Universidad Autónoma de San Luis Potosí, Av. Karakorum #1370, Col. Lomas Altas 4a. sección, CP.78100, San Luis Potosí, S. L. P., México

R. Silva-González

Instituto de Física "Luis Rivera Terrazas," Benemérita Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue., México, C.P. 72570

E. Gómez

Centro de Investigacion en Dispositivos Semiconductores, IC-BUAP Apdo. Postal 1651, Puebla, Pue., México., C.P. 72000

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We have analyzed spark-processed porous GaAs (spp-GaAs) samples prepared by the application of high-voltage discharges at low repetition rates (20 Hz) in different ambients, ranging from pure nitrogen to pure oxygen flow, using a microRaman probe and a scanning electron microscope in combination with an energy dispersive spectroscopy system (SEM-EDS). We found that for samples prepared in pure nitrogen, the resulting material is basically amorphous material, with amorphous-GaAs with some cubic phase of As₂O₃ also present. For samples prepared under even a low concentration of oxygen, 20:1, we find that the cubic phase of As_2O_3 is substituted by the monoclinic phase of As₂O₃ "claudetite." SEM micrographs show the resultant morphologies obtained that exhibit a porous, granular, agglomerated granular appearance. EDS and Raman suggest that the claudetite phase of As_2O_3 and As_2O_5 play a contributing role in the green-blue photoluminescence emitted by spp-GaAs. © 2001 American Vacuum Society. [DOI: 10.1116/1.1366709]

I. INTRODUCTION

In recent years, porous materials have attracted considerable interest because of the discovery that porous Si (p-Si) photoluminesces¹ in the visible spectrum and because this phenomenon may be produced by confined electrons in nanometer-sized granules or pillars in the p-Si.² Spark processing (SP) is a useful alternative for preparing new photoluminescent semiconductor porous materials.³ SP has some potentially desirable features compared to the electrochemical etching method that has been extensively used in silicon.¹⁻³ For example, (a) it is a non-wet approach that could be used to prepare optoelectronic devices; (b) the luminescent area affected can be chosen at will, (c) the emission can be tuned in some materials by changing the parameters of preparation (wafer-tip separation, substrate temperature, ambient gas, pressure, spark frequency, current, voltage, and exposure time) and, (d) the same equipment and procedures can be used for the preparation of any type of semiconductor material.

The list of materials spark processed, whose luminescent properties have been observed and reported in the literature are: Si, Ge, GaAs, Sb, Bi, Sn, As, and Te,⁴ to this list, the semiconductors CdTe, GaSb, InSb, and InP have recently been included.^{5,6}

Recently, several reports have been published on the light-emission properties of porous GaAs prepared by the spark process,^{7–9} as well as of the electrochemically etched porous GaAs (eep-GaAs).¹⁰ The spark-processed porous GaAs (spp-GaAs) prepared at low-frequency sparking shows reproducible photoluminescence (PL) in two main bands: a green-blue band between \sim 2.2 to 2.6 eV and a blue-violet band centered at 3.1 eV.^{8,9} In both works, the green-blue PL is attributed to luminescence from oxygen compounds; x-ray phtololuminescent spectroscopy (XPS) spectra reveal the presence of As₂O₃, As₂O₅, and Ga₂O₃; and the assignment of the PL to the arsenic oxides is made.⁹ This assignment is confirmed by some preliminary Raman work included in that work. However, it is not dismissed that the blue-violet emission at 3.1 eV may be due to confinement effects. In Ref. 10, the PL in eep-GaAs that appears in two bands centered at 2.02 and 2.26 eV is directly correlated to similar emissions from As₂O₃ and As₂O₅, respectively.

In this work, we present a more comprehensive Raman scattering and scanning electron microscope in combination with an energy dispersive spectroscopy system (SEM-EDS) study that reconfirms the presence of both types of arsenic oxides $(As_2O_3 \text{ and } As_2O_5)$ in all samples under study, and the fundamental role that they play as the source of the green-blue PL in air-processed spp-GaAs. Additionally, we obtain results that suggest that in nitrogen-prepared (spp-GaAs), the emissions centered at 2.45–2.55 and at 3.1 eV seem to have their source in material now in an amorphous states as suggested by Raman spectra. As₂O₃, also detected in the Raman experiments in the N-spp-GaAs, appears to be formed during the spark processing by incorporation of some oxygen residual in the sample preparation chamber.

^{a)}Electronic mail: hnavarro@cactus.iico.uaslp.mx