ELSEVIER

Materials Science and Engineering B 130 (2006) 49–56

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Influence of semiconductor surface preparation on photoelectric properties of Al–Zn_3P_2 contacts

Nella Mirowska [*], Jan Misiewicz

Institute of Physics, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland

Received 21 November 2005; accepted 8 February 2006

Abstract

The Schottky barriers formed by Al on Zn_3P_2 p-type crystals have been studied. Three types of crystals (monocrystal, large-grain crystal and polycrystal) were used for device fabrication. The samples were separated in two groups according to the type of structure and the methods of surface preparation. The samples from the first group were different in structure (monocrystal, large-grain crystal and polycrystals) but prepared in the same way. Three polycrystals with differently prepared surfaces were collected in the second group. Two samples from this group were also annealed in open air at 523 K for 24 h. Measurements of photovoltaic effect at room temperature were carried out to test the impact of surface preparation on photoelectric properties of Al–Zn_3P_2 contacts. Substantial differences in shape and intensity of PV signal were observed depending on whether the surface of semiconductor was mechanically polished, chemically etched or/and heat treated. The height of potential barrier, Φ_B, and optical transitions in semiconductor were determined. The value of Φ_B changed from 0.747 to 0.767 eV for unheated samples and from 0.724 to 0.755 eV for the heated ones. The quality of semiconductor surface seems to have an essential influence on spectral characteristics of Al–Zn_3P_2 junctions, especially in the case of polycrystals. It appeared that thorough preliminary mechanical polishing of crystals surface provides quite good photoelectric properties of Al–Zn_3P_2 junctions.

Keywords: Al–Zn_3P_2 junction; Photovoltaic effect; Surface condition; Interface layer

1. Introduction

Zinc phosphide, Zn_3P_2, fulfils the criteria for low-cost high-efficiency solar energy converter [1]. Zn_3P_2 is a p-type semiconductor compound with energy gap ($E_g \sim 1.5$–1.6 eV) close to the optimum value for photovoltaic solar cells and long wavelength optoelectronic devices [2]. The optical properties and inter-band transitions in Zn_3P_2 were presented in [3,4]. The minority carrier diffusion length in Zn_3P_2 is relatively long (~10 μm), what permits high conversion efficiency [5,6]. The hole concentration in this compound is in the range of 10^{12}–10^{16} cm^{-3}, the carrier mobility is equal to 20 $cm^2 V^{-1} s^{-1}$, and resistivity, $\rho = 10$–10^3 Ω cm [5,7]. For these reasons the photoelectric and electric properties of metal–Zn_3P_2 Schottky diodes have been investigated in our laboratory for many years. Among various metals (Mg, Al, In), which can form an active contact to Zn_3P_2, only Mg–Zn_3P_2 junctions were intensively studied [5–8]. Al–Zn_3P_2 diodes, fabricated on bulk crystals, have not been sufficiently examined so far [6,9,10]. The potential barrier Φ_B of the height in the range of 0.7–0.8 eV for Al–Zn_3P_2 and 0.81 eV for Mg–Zn_3P_2 was reported in [10]. At present, the preparation of Zn_3P_2 thin films and investigations of diode made on them is more of interest [11–14] than diodes made on bulk crystals. However, an electrical preliminary study of Al–Zn_3P_2 bulk crystals was presented in [9]. The barrier height Φ_B in the range of 0.3–0.4 eV is reported in that paper. It was obtained for samples chemically etched in 3% bromine methanol solution. More recent investigations were carried out for samples additionally etched in H_2O:HCl (1:1) solution and the higher value of $\Phi_B = 0.67$–0.76 eV was obtained. The different mechanisms of barrier formation for Al and Mg were also suggested in [1].

The purpose of our work was to study the photovoltaic properties of Al–Zn_3P_2 junctions. Photo-voltage spectra (PV) were measured at room temperature for samples before and after heat treatment. Prior to device fabrication the surface of each Zn_3P_2 crystal was intentionally prepared in different way. The effects of surface preparation and samples heating on proper-

---

[*] Corresponding author. Fax: +48 71 328 36 96.
E-mail address: nella.mirowska@pwr.wroc.pl (N. Mirowska).

0921-5107/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mseb.2006.02.043

ties of Al–Zn_3P_2 junctions are discussed. The barrier height and optical transitions were determined.

2. Sample preparation and experimental details

Zn_3P_2 crystals were grown by using a closed-tube vertical vapour transport [16]. Two groups of Al–Zn_3P_2 Schottky diodes were prepared.

The first group of samples was used in preliminary studies. Three wafers of monocrystal, large-grain crystal, and polycrystalline of irregular shape were selected. The method of surface preparation was the same for all samples. At first, they were mechanically polished with Al_2O_3 powder of decreasing grain size (0.9, 0.7 and 0.05 μm) till mirror-smooth surface was obtained. Next, the wafers were rinsed in methanol and chemically polished in 5% bromine methanol solution for 5 min. Just before electrical contact making, the sequence of degreasing processes in methanol, trichloroethylene, acetone and methanol was done for each wafer. Semitransparent electrical contacts (Al and Au), rectangular in shape, were prepared by 10^{-6} Torr vacuum evaporation of pure metals on the front side of wafer. The deposition was made through a metal mask. The hole concentration, N_p, of obtained samples was equal to $\sim 10^{13}\,\mathrm{cm}^{-3}$ (polycrystalline—JXIII), $\sim 5 \times 10^{15}\,\mathrm{cm}^{-3}$ (large-grain crystal—1309) and $\sim 10^{15}\,\mathrm{cm}^{-3}$ (monocrystal—0789).

The second group of more thoroughly investigated samples were polycrystalline crystals of Zn_3P_2 prepared in different way. Parallel slices of the thickness of about 900 μm were cut out from the boules, mechanically polished with Al_2O_3 powder and degreased in methanol. Three wafers, ZP0, ZP1, ZP2, of half-round shape, with differently prepared surfaces were selected. ZP0 wafer was polished with powder of decreasing grain size 0.9 and 0.7 μm. ZP1 and ZP2 were polished with 0.9, 0.7 and 0.05 μm grain size powder until a mirror-smooth surface was obtained. After polishing each wafer was rinsed in methanol. ZP2 was additionally etched in 5% bromine methanol solution for 5 min. Final processes of degreasing and electrical contacts preparation were identical with the method used for samples from the first group. Rectifying Al contact, front side to each wafer, and ohmic Au contacts, front and back, were evaporated. Due to such localization of Au contacts it was possible to check their ohmic character. The distance between front contacts of width of 0.1cm was equal to 0.236, 0.293 and 0.361 cm for ZP0, ZP1 and ZP2, respectively. Final thickness of ZP0, ZP1 and ZP2 samples was 850, 840 and 815 μm, respectively. All contacts parameters (area, width, front electrode spacing), samples thickness and sample surface preparation methods were collected in the Table 1.

The hole concentration of examined samples was equal to $\sim 6 \times 10^{14}\,\mathrm{cm}^{-3}$ (ZP0), $\sim 10^{14}\,\mathrm{cm}^{-3}$ (ZP1) and $\sim 2.5 \times 10^{13}\,\mathrm{cm}^{-3}$ (ZP2). It was obtained through the use of electrical transport measurements.

All investigated devices, from the first and the second group, were prepared without any antireflection coating.

Spectral measurements were performed at room temperature in the dark with a semi-automatic experimental arrangement based on the SPM-2 Zeiss monochromator and lock-in system [17]. The 150 W halogen lamp (tungsten lamp) was used as a source of light. The light beam was chopped with 12.7 Hz frequency. As a reference detector we used the Vth-1 Zeiss thermocouple with constant spectral sensitivity in the wide wavelength range. This arrangement allowed us to obtain directly the ratio of the examined contact photoresponse to that of the thermocouple, i.e. the relative photovoltaic (PV) signal. The sample, thermocouple and a set of mirrors were placed in a special chamber guarantied a good blackout and shielding during measurements. With the help of such a measuring set-up even a very weak PV signal could be detected and measured after amplification.

The photovoltaic (PV) signals of Al–Zn_3P_2 structures were recorded in the wide wavelength range of 1.95–0.4 μm (i.e. 0.65–3.0 eV). An intensive PV signal was observed within the energy range of 1.2–2.5 eV. The measurements were carried out in a few configurations of lighting spot-versus-contact position on sample surface. The monochromator slit was different for different samples but for most of them it was equal to 0.5 mm. Thus, all the recorded curves were normalized to 0.5 mm slit width. Different amplifications of measured PV signals for samples from the second group were also included in this normalization. The intensity of measured PV signals could be compared within each group of samples.

After measurements of PV and current–voltage (*I–U*) characteristics for ZP0, ZP1 and ZP2 samples, two of them (ZP1 and ZP2) were annealed. Thermal annealing was carried out in open air at 523 K for 24 h, after precise rinsing the specimens in methanol. For annealed samples the PV and *I–U* measurements were repeated.

The dark current–voltage (*I–U*) characteristics were performed in the voltage range of about (−3 to +3) V at room

Table 1
Methods of surface preparation and dimension data of Zn_3P_2 samples

Sample number	Surface treatment [grain size in (μm)]	Sample thickness (μm)	Al contact (semitransparent)		Front electrode spacing (cm)
			Area (cm^2)	Width (cm^2)	
ZP0	Mechanically polished [0.9 and 0.7]	850	0.0297	0.1	0.236
ZP1	Mechanically polished [0.9; 0.7; 0.05]	840	0.0156	0.1	0.293
ZP2	Mechanically polished [0.9; 0.7; 0.05] and etched in 5% Br/MeOH	815	0.0297	0.1	0.361