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VACUUM PHOTOTHERMAL PROCESSING (VPP) FOR CURING OF THE COMPLEX THIN FILM SYSTEMS

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Vacuum photothermal processing (VPP) of complex thin films is reported. The thermal process is based on exposure of thin films systems such as Al-Al_2O_3-Ge-Au and In_2O_3 deposited on glass substrates, to a non-coherent radiation of a tungsten coil heated to about 3000 ^0C in vacuum. This process is different from the conventional Rapid Thermal Processing (RTP) that uses glass sealed light sources as heaters, due to the significant role of high energetic photons. The experimental data indicate a decrease in the sheet resistance value of transparent conductive In_2O_3 thin films from about 1,000 Ω/Sq to an average resistance of 120 Ω/Sq. Another result is the increase of the film's homogeneity following the VPP treatment. VPP processing of semiconductor structures produces a healing effect in the crystalline lattice that has undergone irreversible breakdown before VPP. Furthermore, a clear shift of the volt-ampere characteristics of the semiconductor Al-Al_2O_3-Ge-Au thin film structure was observed after VPP: The system's resistance changes from 2.25 Ω to 0.76 Ω and the conduction voltage increases from 1.3 V to 3.3 V.

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1. Introduction

The ever growing development of sub-micron devices such as ULSI, micro-machines, multi-quantum well solar cells, etc., demands a continuous reduction in the macroscopic and microscopic defects during the manufacturing process. These defects are caused by various atomic mechanisms. For example, ion implantation leads to the appearance of crystal damage. At the end of the implantation process it is necessary to re-locate the implanted ions and displaced atoms onto the active lattice sites. This re-location is done in what is called "a post-implantation annealing process".

The traditional annealing process, "a furnace process", is done by heating the silicon wafers in a furnace at ~1000 °C for up to a few hours. Not only is this process time consuming, but it is not appropriate for complex semiconductors such as III-V or II-VI compounds having a comparative low dissociation temperature and high vapor pressure of the V or VI element groups.

Furnace processing was used for a long time and included a number of steps in the semiconductor manufacturing industry. However, modern devices require low temperature processing, low thermal and residual stress, small amount of defects and faster processes with high yields and throughputs.

The fundamental disadvantages of furnace processes were removed with the introduction of "Rapid Thermal Annealing" (RTA). The first RTA process was demonstrated in 1975 [1] by using pulsed lasers to anneal ion implanted GaAs devices. Many different types of RTA methods for transient annealing were proposed since then, though first RTA application were described in 1980 [2, 3]. All of these methods were based on the application of different types of heating lamps or lasers on the annealed substrate. In this paper we report the experimental results obtained in a new approach called Vacuum Photothermal Processing (VPP) and based on fast irradiation in vacuum of thin films.

This approach is based on the RTA process principles and relates the changes in the electric properties of the semiconductor films to photonic effects rather than to thermal effects.

2. Basic principles of rapid thermal processing

The basic idea behind the RTA is the exposure of semiconductor samples to a radiation flux generated by arc or halogen lamps. One or two banks of halogen lamps above and below irradiate the wafer while providing nitrogen ambient in the reaction chamber in order to stabilize the vapour pressure [4]. The power to the water-cooled lamps is computer controlled via a negative feedback loop. In the old configuration of the RTA a thermocouple on a calibration wafer was used as a temperature sensor. However, most of the modern RTA systems are using a pyrometer for a direct measurement of the heated wafer temperature. Typical RTA processing period is 2 to 10 seconds at temperatures between 800-1050 °C for implants in GaAs. Modifications of this technique may include several numbers of lamp banks and several numbers of lamps in the bank. Other arrangements of the lamp's structure may also have an influence on the final properties of the treated sample [5].

The Rapid Thermal Processing (RTP) is based on an incoherent radiation from lamps such as tungsten or halogen [6]. This procedure combines annealing process as well as photonic influence. Furnace process caused by photons of infra-red diapason with wavelengths longer than 0.8 μm. Irradiation of samples with photons of short wavelengths (visible range and UV diapason) permits decrease a treatment period as well as annealing temperature of samples. In the case of the RTP the short wavelength photons influence becomes more significant than heating waves. According to the Plank's radiation low [7], the maximum of the spectral radiation distribution shifts to the shorter wavelengths part of the spectrum for higher intensities of black bodies. The tungsten filament in the halogen lamps is heated up to 3000° K approximately so that most of the RTP treatment is done by the shorter wavelength photons, that is, photons with energy that ranges from the ultraviolet to the visible range. Evidently, the influencing mechanisms of long wavelength photons and short wavelength photons on semiconductors are different from each other. Authors of the fundamental work [8] showed: owing to quantum effects an incoherent light results with a short RTP impact, which brings reduction in the activation energy, reduction in the surface roughness and improvement of the uniformity of the process annealing.

Halogen and deuterium lamps, when used as sources for incoherent light, decrease the influence of thermal effects and increase the role of the quantum effects on the sample being processed. Also it was shown [8] that application of the deuterium lamp only (vacuum UV source) with intensity of 10 mW/cm^2 does not increase the temperature of the wafer (purely quantum effects). In addition, RTP leads to cardinal transformations in the structure of the contacts and its type in the metal-semiconductor system of Ti-Al-GaN. It was shown [9] that RTP in Ar atmosphere changes the contact type from non-linear to ohmic with a specific contact resistance of approximately 10^{-2} Ω/Sq owing to reaction between Al an Ti.

3. Experimental setup

Fig. 1 presents a principle scheme of our experimental setup. A standard tungsten coil evaporator [10] was used as an energy source. This tungsten coil is braided of four pure tungsten wires, each of them 1 mm in diameter, and ~ 37.5 cm long. The treated samples were placed 30 mm far from the coil. During the VPP the temperature of the samples was measured by a thermocouple (K-type - Cromega-Alomega). ACA Leakage Tester type DL-6054 measured the current through the tungsten coil. Also, the voltage drop on the tungsten coil was measured. These data were used for the estimation of the energy source temperature. The composition of the deposited films was evaluated using the Energy Dispersive Spectrometry (EDS) mounted on the STEREOSCAN-430 (LEICA Scanning Electron Microscope operating in 20 keV). Film thickness was measured with an automatic

"Tencor Instruments" profilometer. A Canon microscope with magnification of up to ×1600 evaluated the sample surface and its structure.

The I-V characteristics of the thin film systems before and after the VPP processing were compared. In addition, the I-V characteristics of the VPP treated samples were compared in order to control them. These characteristics were obtained using a Keithley bench station.

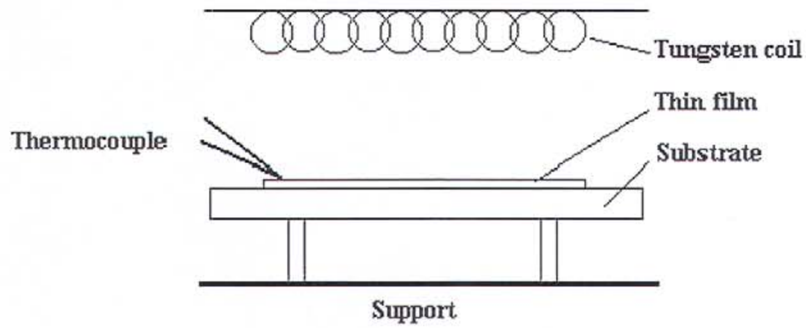

Fig. 1 Schematic set-up of vacuum photo-thermal processing.

3.1 Sample preparation

The VPP was applied to the 4 mm^2 samples of glass-Al-Al_2O_3-Ge-Au systems. Fig. 2 presents a typical thin film structure of a measured sample. This structure consists of crosswise disposed electrodes and the semiconductor films between them. The size of the samples with transparent conductive coating of In_2O_3 on the glass substrates was 25×75 mm^2.

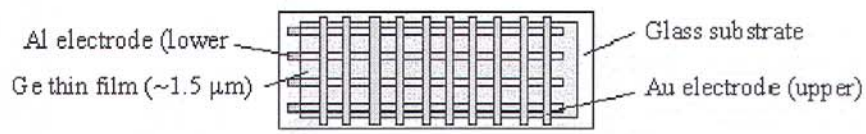

Fig. 2 Typical structure for I-V characterization.

A thin film of Al_2O_3 is a natural oxide that grows on the lower electrode when vacuum is broken. The use of a magnetron sputtering vacuum station [11, 12] enabled to grow germanium and indium oxide semiconductor thin films. The thickness of the Ge films was ~ 1.5 μm. The thickness of the grown In_2O_3 transparent conductive thin films was found to be about 250 nm [13].

3.2 Control experiments

It is found that the temperature of the samples during the VPP raises up to about 400 °C (see Fig. 3). Therefore, in order to verify that the treatment is performed by photons and not by thermal effect it is necessary to control the process such that thermal effect be eliminated.

This control was done in two ways in the present work. In one control experiment similar samples were heated up by a hot plate to 400 °C for the same period of time as in the VPP, and the electrical properties of these samples were compared to samples that were treated with the VPP. In a second control experiment a glass with absorption edge at 380 nm was introduced between the tungsten coil and the samples. This glass blocked the UV light from reaching the sample and therefore the samples were exposed only to thermal effects and to photons in the visible range. Like in the first controlled experiment the electrical properties of these samples were compared to those of the VPP treated samples.

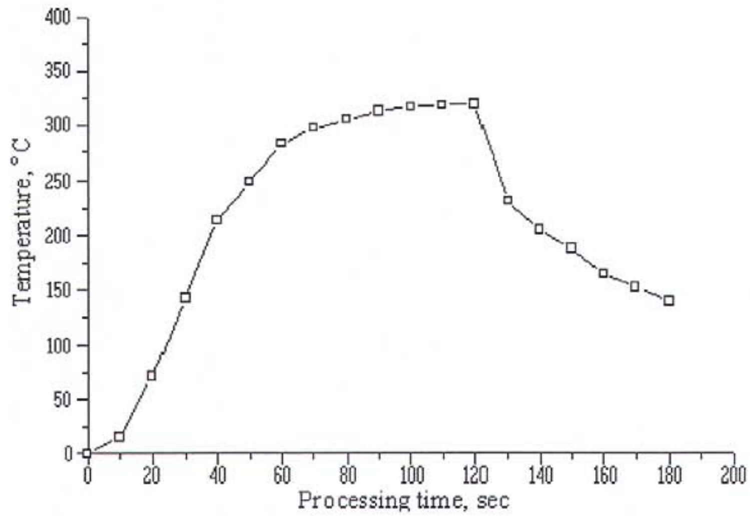

Fig. 3 Typical vacuum photothermal processing.

4. Results and discussion

Fig. 4 shows the samples surface temperature for various VPP periods. All of the VPP experiments with several thin film systems were found to be reproducible. Highly important for the VPP process is the temperature of the energy source. It is well known that tungsten coils may be heated up to ~3000° K in vacuum for long periods [14], since its melting point is ~ 3683° K and boiling point is ~ 6200° K [15].

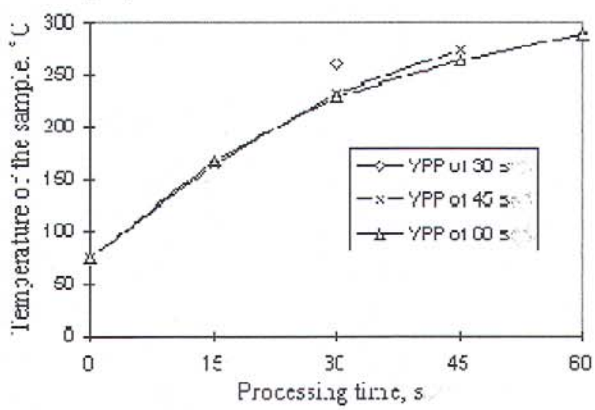

Fig. 4 The dynamics characterization of VPP processing.

Fig. 5 illustrates the tungsten vapor pressure for high temperature [16]. One can see that practically up to the melting point the tungsten is not evaporated (the vapour pressure is less than 10^{-2} Torr). The temperature of the tungsten coil was estimated using current and voltage drop measurements. Typical time dependence of the temperature source appears in Fig. 6. Average measured values of these parameters were as follows: I = 52.4 A (current), U = 6.61 V (voltage drop).

The temperature estimation of the tungsten coil on its surface was ~ 3363° K. For the calculation we applied the standard data of the dependence of tungsten resistivity on temperature [17].

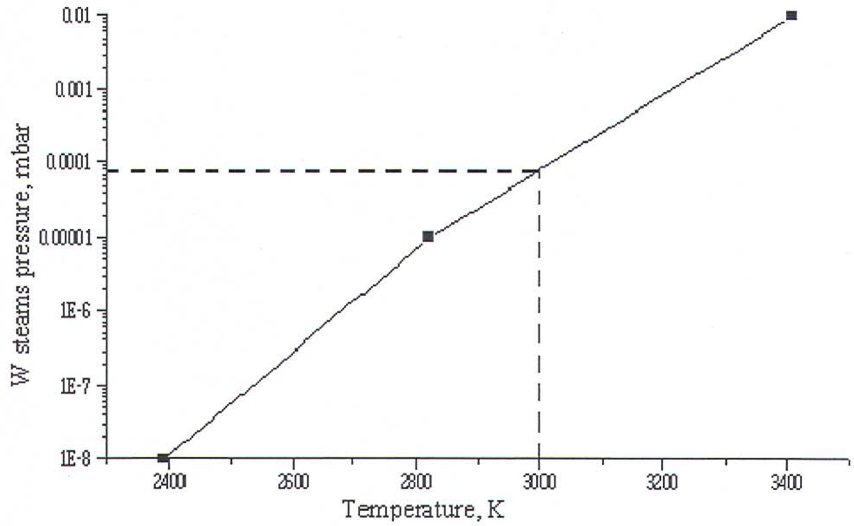

Fig. 5 Tungsten steams pressure [16].

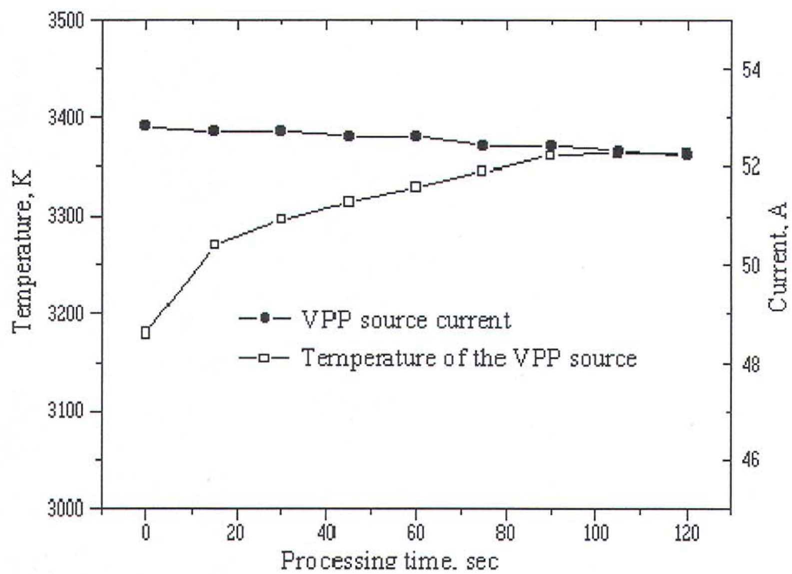

Fig. 6 Tungsten coil temperature during VPP.

These data and the interpolation formula are shown in Fig. 7. The quantity of photons used in irradiation and provided by the annealed tungsten coil was evaluated as the ratio of irradiation intensity (I_λ) to energy of photons (E_λ). In turn, irradiation intensity was calculated accordingly to the well-known Planck's relation [18].

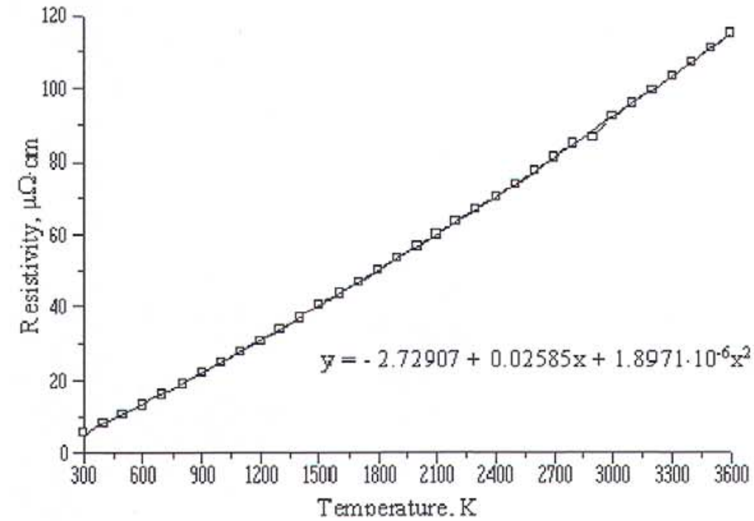

Fig. 7 Tungsten resistivity dependence on the temperature [17].

Here h is the Planck's constant, c is the speed of light, k is the Boltzmann's constant, λ is the wavelength. The estimated data are presented in Fig. 8. The comparison between the tungsten coil and the known calibrated sources of "McPherson Inc." [19] shows a more simplified and higher power (~ 350 W) for the proposed process than the standard lamp application. Tungsten-Halogen light source of the mentioned company is a high-energy lamp of 100 W. This source generates an intense continuous spectrum from 400 nm to 2 microns. Therefore, one can say that by using free of jacket tungsten coils the process may become more efficient and radiation with higher intensity is produced. There are, of course, several specific light sources for vacuum ultraviolet and open-air ultraviolet such as deuterium lamps. These sources provide a continuous spectrum ranging from 115 to 370 nm. However, the thermal effects are completely eliminated in this case.

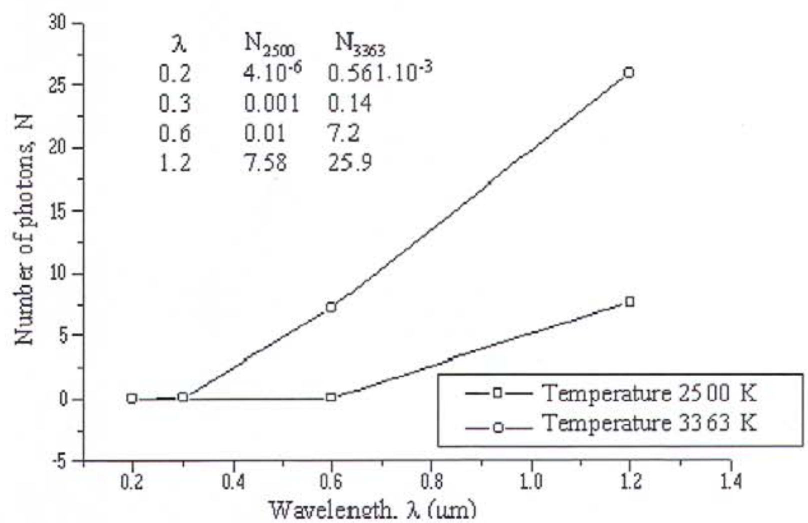

Fig. 8 Spectral efficiency of tungsten for different temperatures.

4.1 The mechanical properties of the films

Fig. 9 presents the microscopic picture of a wedge section in the glass-Al-Al_2O_3-Ge-Au system. Germanium thin film surface obtained by sputtering represents a very non-homogeneous face as shown in Fig. 10 [12]. This nano-crystalline structure was obtained with the following technological parameters:

- Residual pressure ~ 3×10^{-5} Torr
- Argon pressure ~ 130 mTorr
- D.C. sputtering voltage - 2 kV;
- Substrate temperature ~ 200° C;

This surface was found to have many surface states that essentially influence the electron transport mobility in the studied system. A rapid thermal processing step has been shown to be a cure mechanism able to produce precise structural phase transformations, including carrier traps removal [20, 21].

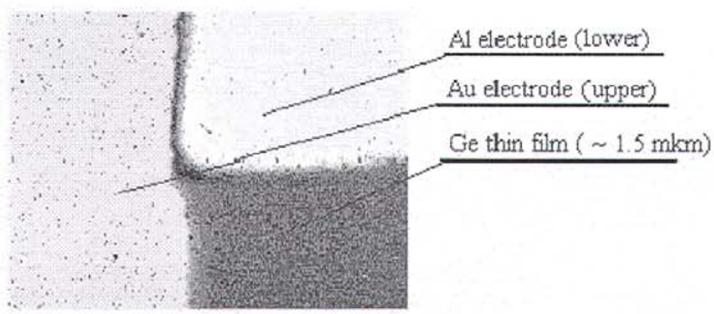

Fig. 9 Microscopic view of the Al-Al_2O_3-Ge-Au system (× 80).

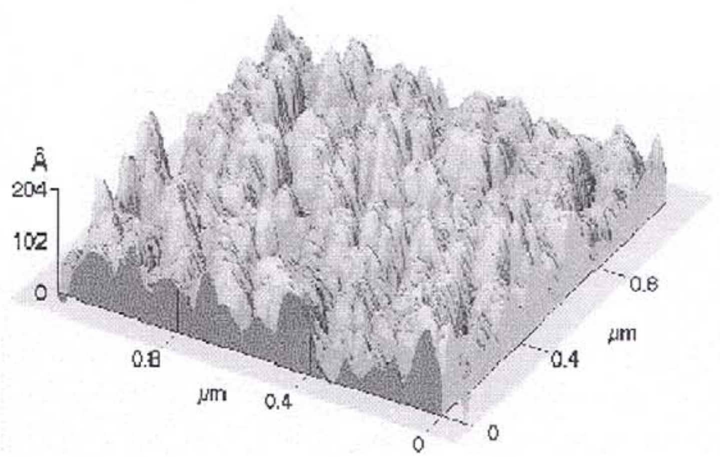

Fig. 10 A 3D presentation of the Ge thin film surface (AFM microscope).

The main three general parameters that mostly influence the properties of the thin film system during thermal processing are film's material, thickness and thermal treatment duration. Vacuum photothermal processing was examined for various processing periods, for various materials and for various thin film thickness. The treatment period was chosen according to the data from Ref. [6], ranging between 15 - 90 seconds. The influence of the thermal processes becomes significant after about 120 seconds of treatment due to the temperature increase of the sample, resulting in higher diffusion rate. For temperatures higher than 400 °C the Au atoms penetrate the semiconductor system and the whole structure is destroyed. Fig. 11 presents a comparative external view of some samples treated by VPP and by the conventional furnace annealing treatment. All samples designated 2b were heated up to 400 °C and were destroyed in a real time measurement due to the different thermal expansion/contraction coefficients of the semiconductor layers and the glass substrate. The thin films were wrecked and part of Au atoms were diffused into the Ge layer. On the other hand, all of the VPP treated samples (1b) kept their shape and form.

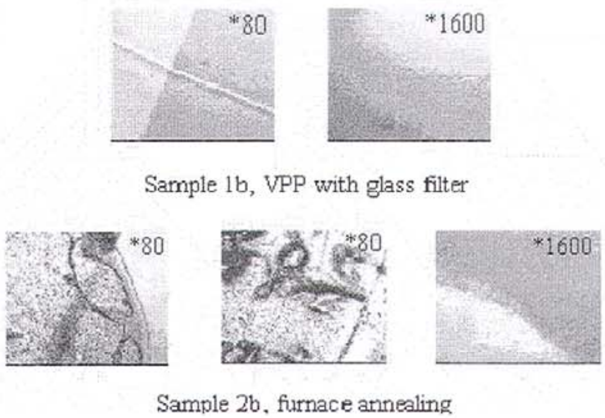

Fig. 11 External view of the processed samples.

4.2 The electrical properties of the films

It is found that the Al-Al_2O_3-Ge-Au system results with Schottky barrier diode characteristics with properties that are affected by the VPP process.

Fig. 12 presents a typical I-V characteristic of the glass-Al-Al_2O_3-Ge-Au system (sample 2a) measured after the deposition and after the hot plate control experiment. It is easily seen that there is no significant change in the electrical properties of the thin film system due to the short-time treatment.

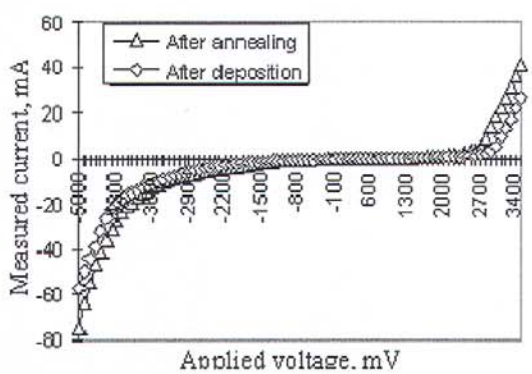

Fig. 12 Electrical property measurements before and after a traditional furnace annealing treatment of the glass-Al-Al_2O_3-Ge-Au system.

Similar measurements were made before and after the VPP process with a glass filter placed between the source of radiation and the sample system. These measurements are shown in Fig. 13. The most significant modification in the electrical properties, presented in this figure, is mainly due to the added tungsten coil radiation in the visible range in comparison with the hot plate control experiment.

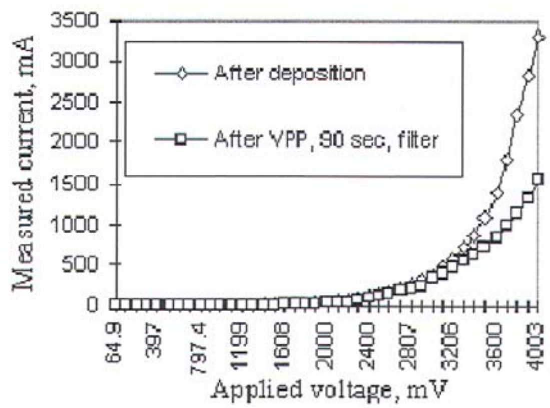

Fig. 13 VPP with glass filter (sample 1b).

Fig. 14 demonstrates the I-V characteristic variations before and after a VPP process. The experiment was done on several typical glass-Al-Al_2O_3-Ge-Au system samples (1A), all grown under the same conditions for the same Ge layer thickness of ~ 1.5 μm. From these results we conclude that shorter wavelengths radiations, which act during the VPP, are responsible for the essential modulation in the film's properties.

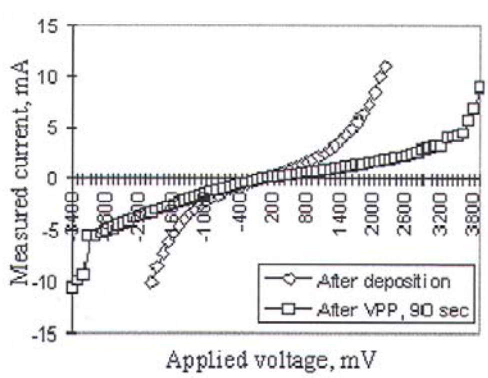

Fig. 14 VPP processing of a glass-Al-Al_2O_3-Ge-Au system.

Fig. 15 presents the sample temperature versus processing time for three types of treatments: filtered VPP, hot plate, and full VPP. It is shown that the temperature of the filtered VPP is approximately equal in all three cases. At the same time the influence on the electrical properties is significantly higher in the full VPP. The longer duration of the hot plate treatment leads to a fatal destruction of the semiconductor film and the measuring system on it. Also, note that unlike the RTP that uses tungsten or halogen (or deuterium) lamps as heat sources, in our case there is no jacket to the irradiating lamps. Therefore, more ultraviolet (UV) photons are involved in the annealing process.

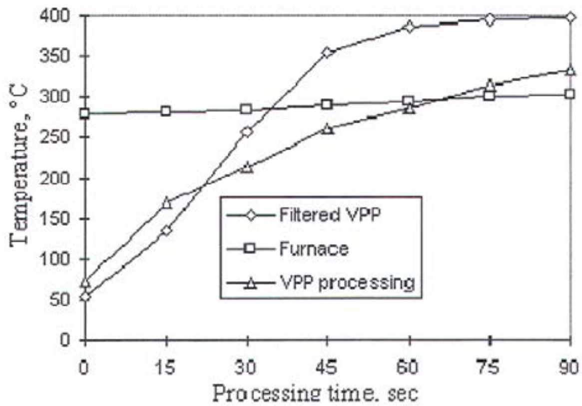

Fig. 15 Samples temperatures vs. processing time for various thermal treatments.

In Fig. 14 VPP leads to an increase in the thin film resistance and an increase in the built-in potential barrier. This phenomenon can be explained as due to excitation of free bonds in the boundary between the metal and the nano-crystalline germanium layers owing to absorbed wavelength photons. On the other hand, the excited surface states are saturated and a potential barrier appears. In other words, the number of free charge carriers in the semiconductor and at the interface between the metal electrode and the semiconductor film is decreased. Furthermore, after the VPP the breakdown point is cured and the breakdown voltage increases.

As shown in Figs. 16 and 17, VPP decreases the sheet resistance and improves the sheet resistance uniformity of the glass-In_2O_3 systems. This effect may be explained by the redistribution of the partially oxidized indium atoms in the oxide film and the partial reduction of indium oxide at the expense of excited electrons under the ultraviolet photon impact. Therefore, the VPP is found to improve the quality of transparent conductive layers.

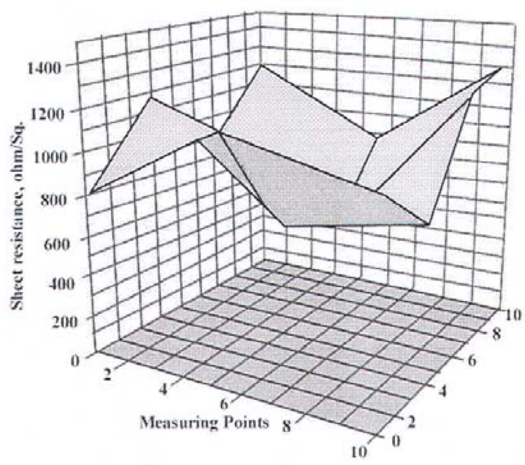

Fig. 16 Sheet resistance distribution of the glass-In_2O_3 system.

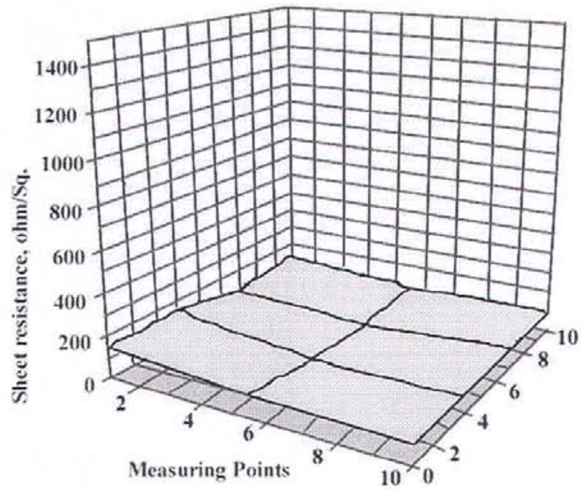

Fig. 17 Sheet resistance distribution of VPP processed glass-In_2O_3 system.

5. Conclusions

This paper present a novel RPP process called Vacuum Photothermal Processing (VPP). This process consists in the treatment of films by exposing them to the radiation emitted by a tungsten coil (filament) and not to heat sources such as halogen lamp with glass jacket. It is shown that heated tungsten coil emits high amount of UV radiation that is responsible for the VPP.

The VPP was used on several samples and it was found to heal lattice points of Al-Al_2O_3-Ge-Au system that had undergone an irreversible breakdown. VPP diminishes the resistance of this system from 2.25 Ω to 0.76 Ω. In addition, VPP was used for annealing the In_2O_3 system. The annealing process decreases the sheet resistance of the film from about 1,000 Ω/Sq to an average value of 120 Ω/Sq and improves the uniformity of the conductivity across the sample.

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