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CARRIER TRANSPORT AND I-V CHARACTERISTIC OF Au/Si SILICIDES USING OPEN PHOTOACOUSTIC CELL AND FOUR POINT-PROBE TECHNIQUES

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ABSTRACT

The carrier transport properties of Au/Si samples annealed at three temperatures (i.e., 100 °C, 363 °C and 800 °C) were investigated using the open photoacoustic cell (OPC) technique. A gold film of 45 nm was deposited on the silicon substrate and annealed in air environment. We observed that $Au_{8.1}Si_{1.9}$ silicide and $Au_7Si(622)$ silicide were formed at both 363 °C and 800 °C annealing temperatures. Obviously the $Au_{8.1}Si_{1.9}$ silicide was observed in all Au/p-Si system. The result indicates that the recombination process increases with the formation of Au_7Si silicide. From the analysis of photoacoustic phase fitting and four point probe techniques, surface recombination velocity of gold silicide was found increase with the increasing annealing temperature. However, the band-to-band recombination lifetime decreased as annealing temperature increased. The I-V characteristic shows the Schottky curves for the annealing temperatures of 363 °C and 800 °C. This behavior is due to the formation of $Au_7Si(622)$ silicide clusters.

INTRODUCTION

A metal/Semiconductor (Au/Si) system is a very interesting model system for understanding the metal/silicide formation. Its properties are important for both the fundamental and technological points of view, especially as metal thin film deposited on Si at temperature well below the processing temperature for Si devices. The (Au/p-Si) system has been studied for better understanding of the interface properties. The Au/Si system is used as a model to study carrier transport properties as well as the I-V characteristic [Kim, 1998]. For this reason, photoacoustic technique was applied because it is simple and reliable method for measuring the thermal and carrier transport properties of metal/semiconductor samples.

In the photoacoustic (PA) technique, absorption of light energy by the sample produces a periodic heat flow in the sample and therefore generates photoacoustic

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signal, which is detected by a sensitive microphone coupled to the cell wall. In the case of semiconductors, the photoacoustic effect does not depend only on optical properties but also on their thermal carrier transport properties (e.g. carrier diffusion coefficient, surface recombination velocity and carrier lifetime) and the non-radiative properties [Neto et. al, 1989]. The absorption of light generates excess carrier distribution in the sample and diffuses through the sample. Then, it is reestablished by desposing the excess energy by both, emitting radiation and by generation of heat. The Photoacoustic technique responds to the fraction of this energy that is converted to heat. There are three heat sources in semiconductors, which arises from the electron-hole collisions within the conduction band (diffusion contribution). The second and the third contributions come from the non-radiative electron-hole pair recombination in the bulk (bulk contribution) and at the surface (surface contribution) [Marin, 2001; Neto et. al, 1989; Todorovic, 2001].

The mathematical expression for the photoacoustic signal in semiconductor samples has been obtained by resorting to the thermal-piston of Rosencwaig and Gersho [Rosencwaig and Gersho, 1976] and it was reported in recent published paper in else where [Yap et al., 2004]. It is well reported that the phase angle ϕ of the photoacoustic signal can be written as:

$$\phi = \phi_o + \Delta\phi \qquad (1)$$

where, ϕ_o is initial phase and, $\Delta\phi = \tan^{-1}\left(\frac{(aD/v)(\omega\tau_{eff} + 1)}{(aD/v)(1 - \omega\tau_{eff}) - 1 - (\omega\tau_{eff})}\right)$

with $\tau_{eff} = \tau[(D/\alpha_s) - 1]$ and $a = (\pi f/\alpha_s)^{1/2}$. Here, D is the carrier diffusion coefficient (cm²/s), v is the surface recombination velocity (cm/s), α_s is the thermal diffusivity (cm²/s), τ_{eff} and τ are the effective recombination lifetime and the band to band recombination lifetime respectively.

In this paper, we report the result of our investigation on the carrier transport and I-V characterization of p-Si wafer, Au/p-Si and Au/p-Si silicide.

MATERIALS AND METHODS

In the present work, p-type polycrystalline Silicon was used as the substrate. It was cleaned by immersing in acetone for one hour. The gold thin film of 45nm thickness was deposited on the polished surface of Si substrate using d.c sputtering system (Edwards SC 7640). Prepared sample was annealed in air at 100°C, 363°C and 800°C for one hour. The measurement was carried out using Open Photoacoustic Cell technique as shown in Figure 1. The sample was placed on the cell and illuminated with a modulated HeNe laser (35mW, $\lambda = 632.8$nm).

The electrical properties of the Au/p-Si sample were then measured using four point probe technique (Jandel resistivity test unit). X-ray Diffraction (XRD) (Philips 7602 EA) was employed to study the formation of gold silicide. The microstructure of the Au/p-Si sample was observed by using Scanning Electron Microscopy (SEM) (Jeol 6400).

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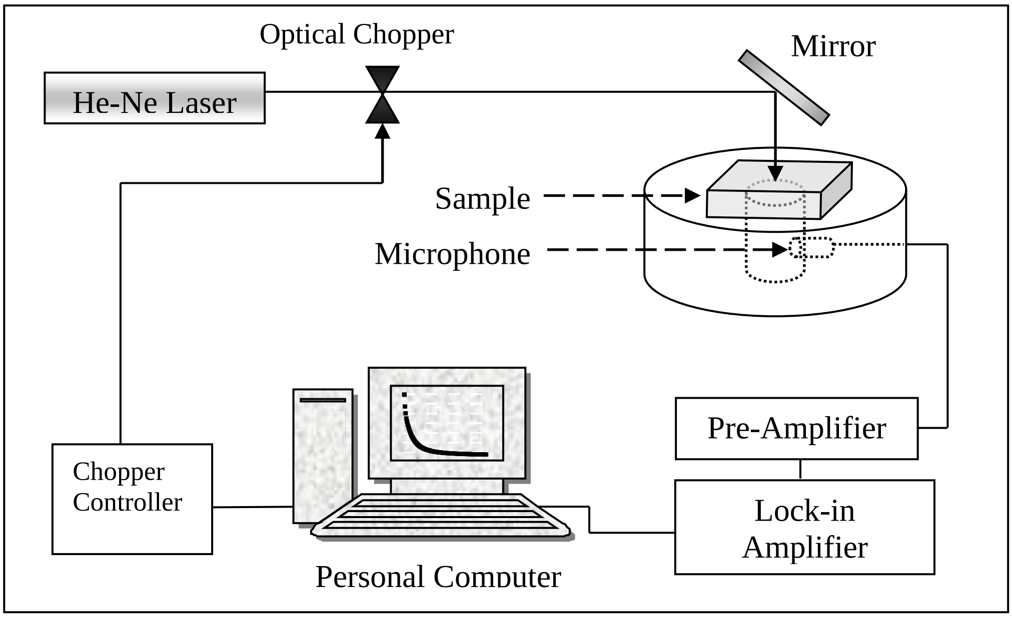
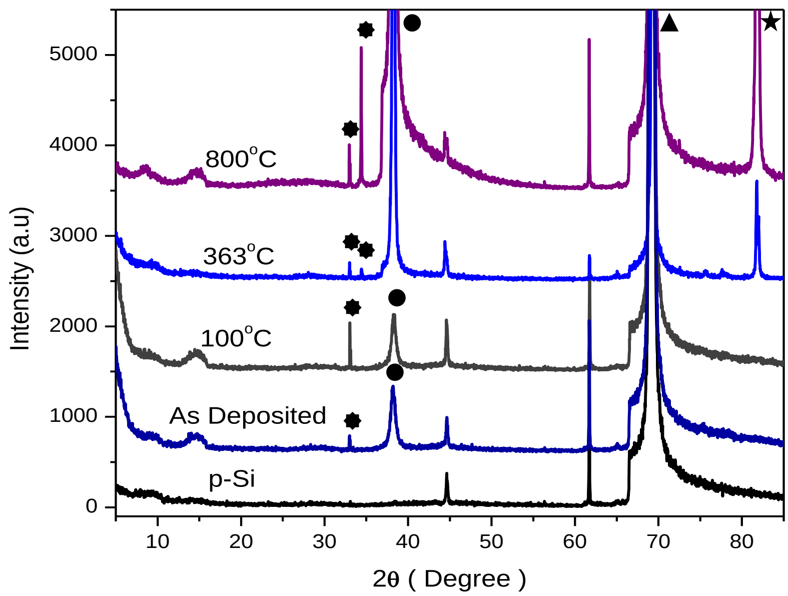


Figure 1: Experimental setup for OPC detection technique.

RESULTS AND DISCUSSION

Figure 2 represents the XRD spectra for Si substrate, as deposited Au/p-Si and Au/p-Si annealed at 100 ^oC, 363 ^oC and 800 ^oC. From the XRD spectra, the peak of $Au_{8.1}Si_{1.9}$ silicide has been observed in all Au/p-Si systems (from room temperature up to 800^{o}C). The Au_7Si(622) (81.73^o) silicide was formed after annealed at both 363^{o}C (eutectic temperature) and 800^{o}C. While, the phase of $Au_{8.1}Si_{1.9}$ silicide also appeared at 34.40^o for the sample annealed at 363^{o}C and 800^{o}C.

Figure 3 shows the best phase fitting for Au/p-Si annealed at 363^{o}C in the thermally thick region using Eq. (1). The same analysis was done for the sample under study. The thermal diffusivity and diffusion coefficient obtained as fitting parameters are shown in Figure 4. As expected, the diffusion coefficient remains unchanged with annealing temperature. However, the thermal diffusivity decreased with increasing annealing temperature. The decreased of thermal diffusivity may be due to the growth of gold silicides clusters and its grain boundary.



● = Au (111), ▲= Si (400) and Si(422), ✸ = $Au_{8.1}Si_{1.9}$ and ★ = Au_7Si (622).

Figure 2: XRD spectra for Si substrate and Au/p-Si annealed at three different temperatures. The deposited gold thin film thickness is 45nm.

Figure 5 shows the surface recombination velocity of the gold silicide samples increases from 408.0 to 596.8 cm/s with the increasing annealing temperature, while, the band-to-band recombination lifetime is decreasing drastically from 9.02 to 4.59 μs. By comparing the XRD spectra (Figure 2) and phase fitting analysis in Figure 5, the surface and bulk recombination process has increased after the formation of crystalline Au_7Si(622) silicide [Neto et al., 1989]. On the other hand, the Schottky curves were observed for sample annealed at 363°C and 800°C are shown in Figure 6. The Schottky curves at these annealing temperatures was formed due to the formation of Au_7Si(622) silicide [Rhoderick and Williams 1988; Li et al., 2003].
Figure 7 shows the SEM images of a smoothness surface of gold thin film deposited on p-Si substrate in which no gold silicide clusters seen in this sample surface. A similar observation was reported by Chang et al., 2003. The $Au_{8.1}Si_{1.9}$ silicide might be formed at the interface of the Au/p-Si system. Figure 8 shows some bubble like inhomogeneous islands having two-fold symmetry were formed at the Au/p-Si sample surface after annealed at 100°C [Chakraborty et al., 2004]. The gold silicide clusters were not seen on the annealed Au/p-Si sample surface. It may form in the Au/p-Si interface as down shadow holes clusters [Chang et. al, 2003; Khramtosa et. al, 1998; Young et. al, 1998].

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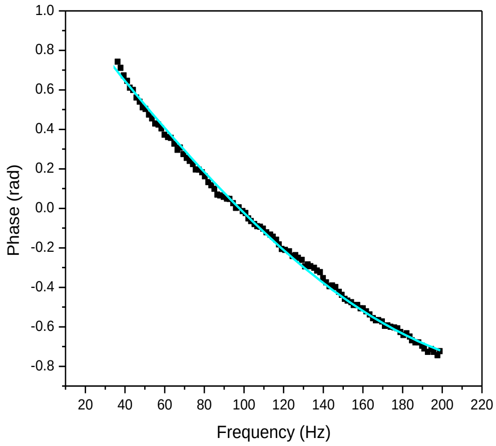

Figure 3: The best phase fitting for Au/p-Si annealed at 363°C for 1 hour.

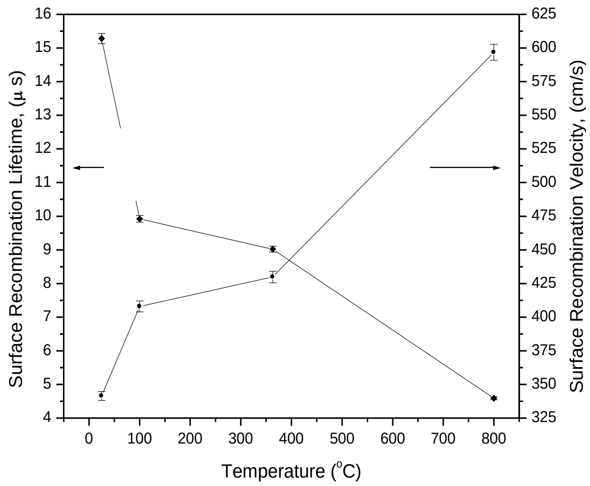

Figure 5: Band to band recombination lifetime and velocity and as a function of annealing temperature.

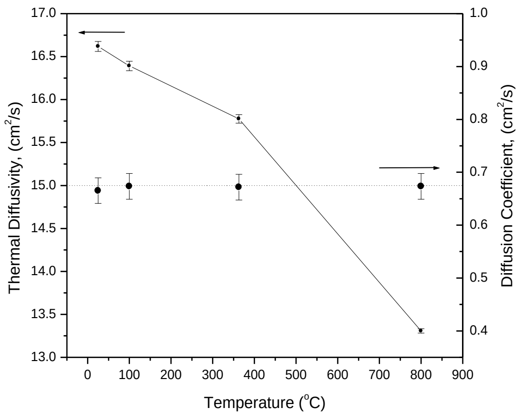

Figure 4: Thermal diffusivity and Diffusion Coefficient versus annealing temperature.

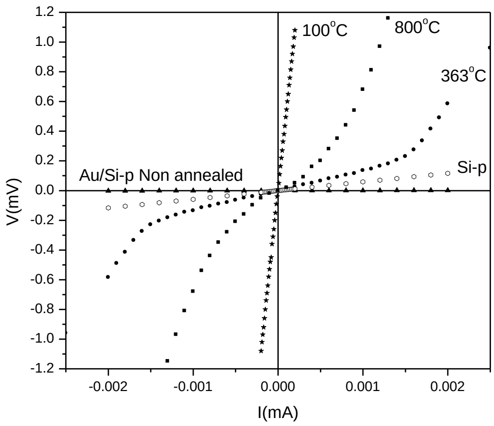

Figure 6: I-V characteristic for Si, as deposited Au/p-Si and annealed Au/p-Si system.

Figure 9 (a) shows that the $Au_{8.1}Si_{1.9}$ silicide and $Au_7Si(622)$ silicide islands homogeneously formed on the surface of Au/p-Si after annealed at 363^oC. We refer this homogeneous silicide islands as a silicide cluster. From Figure 9 (b), the small sphere shape of $Au_{8.1}Si_{1.9}$ silicide clusters as viewed at 45^o shown clearly growth on the sample surface. In addition, we also observed the growth of cylinder shape of Au_7Si silicide and some features like ring-like walled gold islands in Figure 9 (c); somewhat like what has recently been observed on Pb/Si(111) system [Chakraborty et al., 2004].

Figure 10 shows the homogenous of gold silicides clusters are formed on the sample surface of Au/p-Si annealed at 800 ^oC. This annealed Au/p-Si sample had produced islands of various shapes: regular hexagon, elongated hexagon and sphere faceted vacancy islands (Figure 10 (b)). This shape transition for gold silicides clusters are another interesting phenomena observed at the annealing temperature of 800^oC. At higher magnification (Figure 10(b)), it can be observed that the hexagonal and cylinder shapes of Au_7Si (622) silicide clusters were formed as a large size than the sphere shape of $Au_{8.1}Si_{1.9}$ silicide clusters. This fact are in agreement with the results reported by Chakraborty at al., (2004) who proposed that a very small changes in the growth temperature can cause a changes in shape and the symmetry of the gold silicides islands or clusters is intriguing. In the present case, a 45^o side viewing of SEM micrograph is shown in Figure 11. This Figure shows that the growth of three-fold symmetry gold silicides clusters on the Au/p-Si annealed system. Interesting to note that the hexagonal shape of Au_7Si (622) silicide clusters were formed much thicker in average than the sphere shape of $Au_{8.1}Si_{1.9}$ silicide clusters. In this annealing process, the higher composition of Si out-diffused into the Au layer across the interface rather than that the Au agglomerated through the Au/p-Si interface [Chang et al., 2003; Young et al., 1998; Chakraborty et al., 2004]. We proposed that the Au_7Si (622) silicide clusters made the carrier recombined more easily at the surface and through the interface, and therefore produced a lower band to band recombination lifetime and high surface recombination velocity. The surface recombination process increased because of the thicker Au_7Si (622) silicide clusters formed among the $Au_{8.1}Si_{1.9}$ silicide clusters.

As shown in Figure 6, the I-V curve of the Au/p-Si system annealed 363^oC and 800^oC are nearly "ideality" of Schottky curves were found at the annealing temperature of. In detail, Au_7Si (622) silicide more contributed to the formation of Schottky curves as compared to $Au_{8.1}Si_{1.9}$ silicide. This fact was in agreement with our assumption before since the electrical path were percolated through small sphere $Au_{8.1}Si_{1.9}$ silicide clusters rather than Au_7Si (622) silicide clusters. Hence, the formation of the Au_7Si (622) silicide clusters may responsible for a Schottky diode junction [Rhoderick and Williams 1988; Li et al., 2003]. This Au_7Si (622) silicide may present as an n^+ substrate and subsequently contact to the p-type Si substrate to formed a p-n junction characterization (i.e. Schottky curve).

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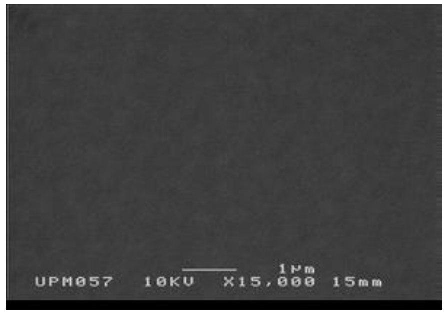

Figure 7: SEM images for the as deposited Au/p-Si sample.

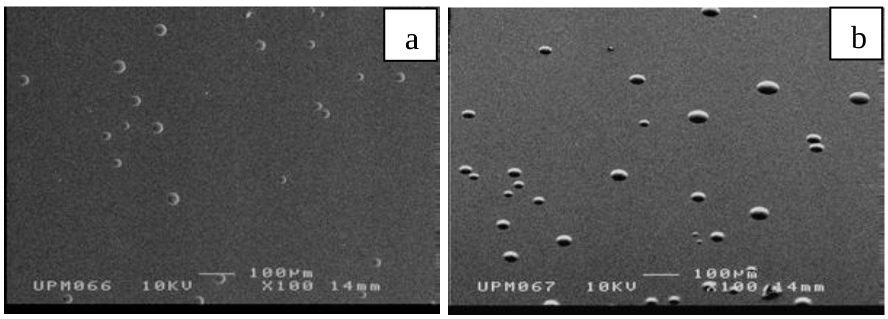

Figure 8: SEM images on Au/p-Si annealed at 100^{o}C for 1 hour. (a) plane viewing and (b) the 45^{o} side viewing.

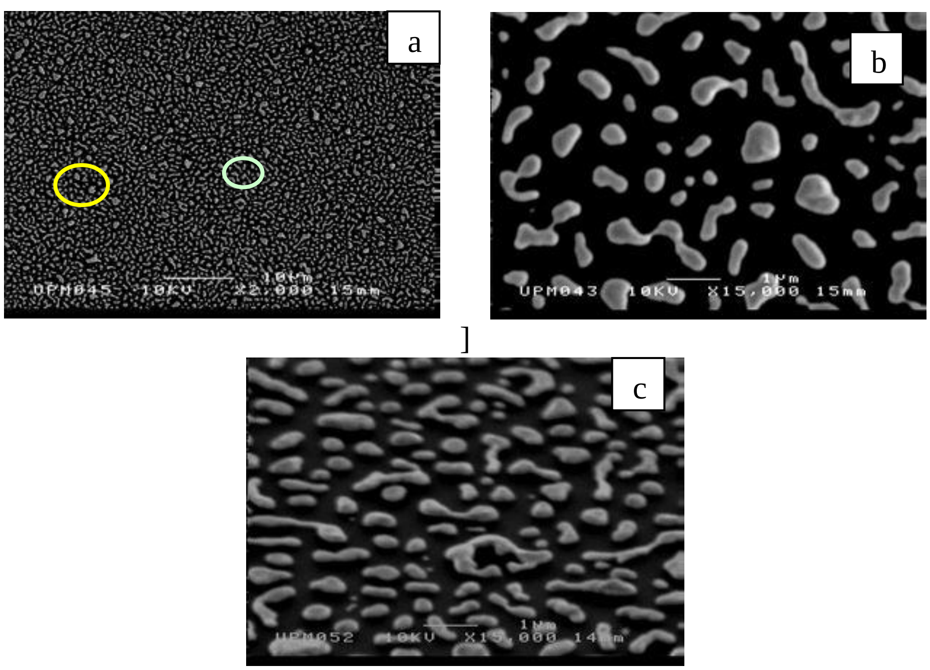

Figure 9: SEM image of Au/p-Si annealed at eutectic temperature, 363^{o}C for 1 hour; (a) x2000, (b) x15000 and (c) 45^{o} side viewing.

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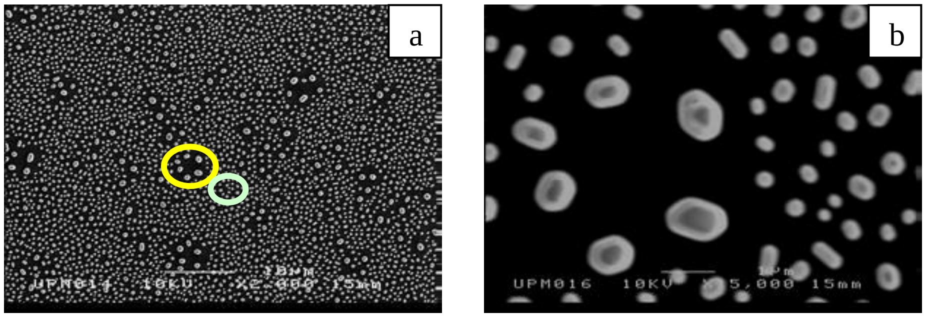

Figure 10: The plane view of SEM images for Au/p-Si after annealed at 800^{o}C for 1 hour; (a) x2000 and (b) x15000

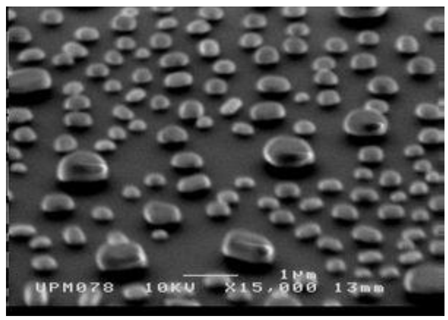

Figure 11: The 45^{o} plane view of SEM images for Au/p-Si annealed at 800^{o}C for 1 hour showing the thicker Au_7Si (622) silicide clusters had formed on the sample surface.

CONCLUSIONS

In short, the surface recombination velocity of gold silicide sample increased and the band to band recombination lifetime decreases as the formation Au_7Si (622) silicide clusters. Moreover, the surface and bulk recombination processes increases with the formation of Au_7Si (622) silicide. The Schottky curves were found at the annealing temperature of 363^{o}C and 800^{o}C. As comparison, the Schottky curves formed contributed more by the Au_7Si (622) silicide compared to $Au_{8.1}Si_{1.9}$ silicide. This is due to the electrical path were percolated through small spheres of $Au_{8.1}Si_{1.9}$ silicide clusters but not Au_7Si (622) silicide clusters. In addition, the Au_7Si (622) silicide may be present as an n^+ compound that contact to the p-type Si substrate and form Schottky curve. Hence, the formation of the Au_7Si (622) silicide clusters produced a Schottky diode junction.

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REFERENCES

[1] Chakraborty, S., J.Kamila, B. Rout, B.Satpati, P.V. Satyam, B. Sundaravel and B.N. Dev. 2004. Shape variation in epitaxial microstructures of gold silicide grown on Br-passivated Si(111) surfaces. *Surface Science*. Vol. 549: 149.

[2] Chang, J.F., T.F. Young, Y.C. Yang, H.Y. Ueng and J.C. Chang. 2004. Silicide formation of Au thin films on (100) Si during annealing. *Material Chemistry and Physics.* Vol 83, Issue 2-3: 199.

[3] Khramtsova, E. A., H. Sakai, K. Hayashi and Ichmiya. 1998. Study of the Si(111)"1x1"-Au surface using reflection high-energy electron diffraction and scanning tunneling microscopy. *Japan Journal Applied Physics*. Vol. 37: 6511.

[4] Kim Y.W., Park N.G., Cho W.S., Chae K.H., Whang C.N., Kim K.S., Kim S.S. and Choi D.S., (1998). Atomic structure of Ag islands on Si(001)(2x1). *Surface Science* 396: 295

[5] Li, M.C., L.C. Zhao and X.K. Chen. 2003. Reducing the effective barrier height of a PtSi Schottky diode by a p^+ doping spike using pulsed laser doping. *Journal Physics D*: Applied Physics. Vol 36: 2347.

[6] Marin, E., I. Riech, P. Diaz and H. Vargas. 2001. On the surface characterization in semiconductor structures using the photoacoustic technique. *Analytical Science*. Vol. 17: s288.

[7] Neto, A.P., H. Vargas, N.F. Leite and L.C.M. Miranda. 1989. Photoacoustic investigation of semiconductor: Influence of carrier diffusion and recombination in PbTe and Si. *Physics Review B*, Vol. 40, 6: 3924.

[8] Rohderick, E.H. and R.H. Williams. 1988. Metal semiconductor contacts second edition. New York: Oxford Science Publication.

[9] Rosencwaig, A and G. Gersho. 1976. Theory of the photoacoustic effect with solids. *Journal Applied Physics*. Vol. 47, 1: 64.

[10] Torodovic, D.M. and M. Smiljanic. 2001. Theory of photoacoustic effect in metal-semiconductor system. *Analytical Sciences*. Vol. 17: s291.

[11] Yap, S.H.,.Mat Yunus W. M. ., Mohd. Maarof M., Zainal A. T., Wan Yusmawati W.Y., Joshephine L.Y.C. , Rosyaini A. Z. and Noor Haslinda D. Surface Microstructure and Carrier Transport Properties of Au/n-Si and Au/p-Si using Open Photoacoustic Technique, Paper presented at 12th Scientific Conference and 13th Annual General Meeting Electron Microscopy Society of Malaysia. *Proceeding 12th Scientific Conference and 13th Annual General Meeting Electron Microscopy Society of Malaysia2003*: 60.

[12] Young, T.F., J.F. Chang and H.Y. Ueng. 1998. Study on annealing effects of Au thin films on Si. *Thin Solid Films.* Vol. 322: 319.