Gold-Free Fully Cu-Metallized InGaP/InGaAs/Ge Triple-Junction Solar Cells

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***Abstract*— Copper contacts and interconnects were developed for GaAs and Ge for low-cost solar cell application. In addition, thermally annealed Pd/Ge and Pt/Ti/Pt metallizations were created for ohmic contacts to n-GaAs and p-Ge with contact resistance of 4.4×10^{-6} and 6.9×10^{-6} Ωcm^2, respectively. Utilizing such metallization structure for InGaP/InGaAs/Ge triple-junction device structure solar cells were fabricated that delivered conversion efficiency of 23.11%, which is average efficiency for the above device structure.**

***Index Terms*— III-V concentrator solar cell, copper metallization, ohmic contact, low cost.**

I. INTRODUCTION

COST effective proliferation of solar cell requires continuous enhancement of its efficiency which in turn leads to panel size reduction. Therefore novel device structures and metallization schemes must be developed for efficiency improvements. Solar cells built on wide band-gap multi-junction structures using III-V semiconductors have yielded highest efficiency as a result of better (~97%) absorption of solar spectrum [1]. Such cells are suitable for thin film format, resistant to radiation damage and lend well with concentrators. In view of these advantages, we have developed InGaP/InGaAs/Ge triple junction solar cells with potential for commercialization. In order to improve the efficiency and its commercialization, we developed several technologies including a new metallization scheme, anti-reflection layer (sub-wavelength structure) [2], new epitaxy layer design (lattice match, current match) [3], utilization of Ge/Si substrate as a replacement for costly p-Ge [4] and cells amenable to concentrator technology. Our metallization scheme involves Cu based contacts, instead of conventional Au based contacts, both as front side interconnects and backside metallization. Further, as reported earlier [5], [6], Pd/Ge/Cu was chosen as contact for n-type GaAs and a novel Pt/Ti/Pt/Cu/Cr metal stack for p-type Ge for this letter. Utilizing fully copper based metallization InGaP/InGaAs/Ge triple junction solar cells were fabricated and their performance is reported here.

For the Pd/Ge/Cu contact, the Pd layer can react with GaAs layer to form $Pd_{12}Ga_5As_2$ [7]. In addition, Ge can alloy with Cu to form Cu_3Ge which is of low resistance and can prevent the Cu diffusion. Furthermore, these two compounds can create the Ga vacancies on the surface of GaAs which allows Ge to diffuse into these vacancies and form a high doping layer without depletion region. This provides easy carrier transport with low contact resistance [8], [9]. On the other hand, for the Pt/Ti/Pt/Cu/Cr contact, the first Pt layer can effectively reduce the barrier height at the interface between the ohmic material and p-Ge substrate since Pt has high work function [10]. In addition, the second Ti layer and third Pt layer can effectively prevent Cu diffusion since Ti and Pt have high melting point. For the interconnect and backside metals, Pt/Ti/Pt was used as the adhesion and diffusion barrier layers and Cu was evaporated as the seed layer after Pt/Ti/Pt deposition. Finally, the Cu layer was electroplated to 5-μm thick. For performance comparison, III-V solar cells with the conventional Au-based interconnects and the n-type Au/Ge/Ni/Au and p-type Ti/Pt/Au ohmic structures were also fabricated on the same GaInP/GaAs/Ge wafer.

II. DEVICE FABRICATION

For solar cell fabrication, n-GaAs epitaxial layer and p-Ge substrate will be the semiconductor layers for contacts on front side and backside of the GaInP/InGaAs/Ge wafer. The samples were first cleaned in a the HCl solution to remove the native oxides and loaded into the evaporator.

For Cu-metallization, Pd (15-nm)/Ge (150-nm) layers were deposited on the n-GaAs contact layer and Pt (5-nm)/ Ti (50-nm)/Pt (60-nm) layers were deposited on the p-Ge substrates by E-gun evaporator.

Then Cu (150-nm) and Cr (10-nm) layers were deposited on top of the two types of interconnects by sputtering. Finally, the front side metal patterns were formed using the lift-off method and the rapid thermal annealed from 100 °C ~390 °C. The samples were annealed for 30 sec in

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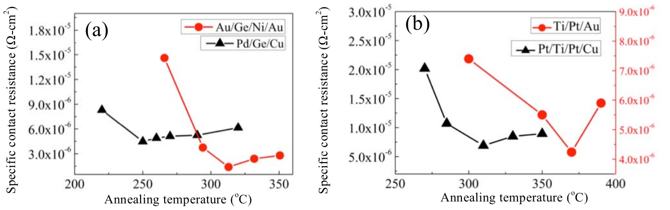

Fig. 1. The specific contact resistance verse annealing temperature curves of (a) n-GaAs and (b) p-Ge ohmic contacts.

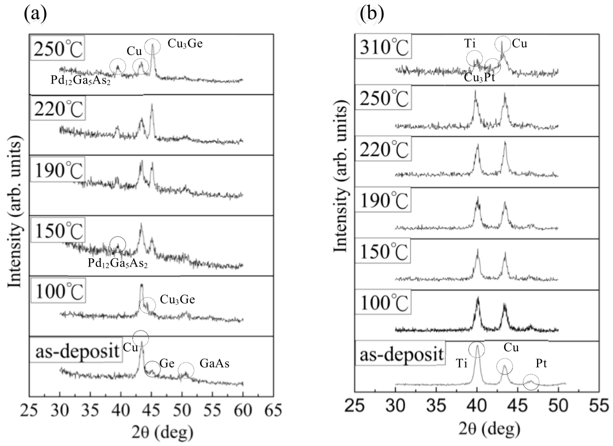

Fig. 2. The X-ray diffraction patterns of (a) n-GaAs and (b) p-Ge ohmic contacts as deposited and after annealing at various temperatures for 30 sec.

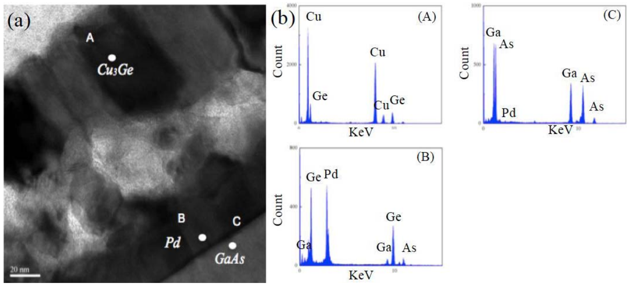

Fig. 3. The (a) cross-sectional TEM image (b) EDX analysis of n-GaAs/Pd/Ge/Cu system.

N2-ambient chamber. Moreover, the III-V solar cells with conventional Au-based interconnects, Au (20 nm)/Ge (40-nm)/Ni (14-nm)/Au (200-nm) and Ti (50-nm)/Pt (60-nm)/Au (250-nm) ohmic contacts, were also fabricated. After the optimization of the ohmic processes, these Cu based ohmic metal systems along with copper interconnects were applied to the development of InGaP/GaAs/Ge solar cells. Finally, fully copper metallized III-V solar cells were evaluated.

The TLM samples were used to optimize the copper based ohmic contact annealing process. The experimental procedures for transmission line model (TLM) sample were performed using 0.5-μm Te-doped GaAs epitaxial layer with doping concentration ND $> 10^{18}$ cm^{-3} and 1-μm B-doped Ge with NA $= 1 \times 10^{18}$ cm^{-3}. The samples were grown by metal-organic vapor phase epitaxy (MOVPE) and high vacuum chemical vapor deposition (HVCVD) on n-i-GaAs (n type GaAs-intrinsic GaAs-GaAs) substrate and p-i-Ge/Si (p type Ge-intrinsic Ge-Ge/Si) substrate, respectively. Standard photolithographic process was used for the Cu-based and Au-based metallized interconnects to define the (TLM) pattern.

III. RESULT AND DISCUSSION

Fig. 1(a) and (b), show the specific contact resistances of n-type GaAs and p-type Ge ohmic contacts, which were treated with different annealing temperatures from 100 to 310 °C. For Pd/Ge/Cu ohmic structure on n-GaAs, the lowest value of specific contact resistance is 4.4×10^{-6} Ω-cm^2 after annealing at 250 °C. For Pt/Ti/Pt/Cu/Cr ohmic structure on p-Ge, the lowest value of specific contact resistance is 6.9×10^{-6} Ω-cm^2 after annealing at 310 °C. Both kinds of Cu-based ohmic contacts have similar performances as the conventional Au/Ge/Ni/Au (1.4×10^{-6} Ω-cm^2) and Ti/Pt/Au (4.2×10^{-6} Ω-cm^2) ohmic contacts.

The formation mechanisms of Cu-metallization ohmic contacts were investigated using TEM and XRD data. The Fig. 2 (a) and (b) show the XRD results of Pd/Ge/Cu and Pt/Ti/Pt/Cu/Cr ohmic contacts. For Pd/Ge/Cu ohmic structure on n-GaAs, the diffraction peaks of $Pd_{12}Ga_5As_2$ and Cu_3Ge were observed after annealing at 100 °C for 30 sec. During the various annealing temperatures from 150 °C to 220 °C, the intensities of $Pd_{12}Ga_5As_2$ peak and Cu_3Ge peak gradually increased, due to the continuous reactions between metal and semiconductor. The TLM result indicate that the ohmic behavior occurred after annealing at 220 °C due to the formation of the Cu_3Ge alloy. After annealing at 250 °C for 30 sec, the intensities of $Pd_{12}Ga_5As_2$ and Cu_3Ge peaks increased significantly, but the intensity of Cu peaks decreased due to the formation of Cu_3Ge alloy. On the other hand, for Pt/Ti/Pt/Cu/Cr ohmic structure on p-Ge, the diffraction peaks of Ti, Pt, and Cu remained almost unchanged even after annealing at 250 °C for 30 sec. However, after annealing at 310 °C for 30 sec, the diffraction peaks of Cu_3Pt started to appear due to the high melting point of Pt. Furthermore, Fig. 3 shows the TEM images and EDX profiles of Pd/Ge/Cu ohmic metal structure after annealing at 250 °C for 30 sec. Fig 3(a) shows the TEM image of the cross-section after annealing at 250 °C. As can be seen from the figure, the Cu_3Ge compound formed vertical grains with long- range order. The grains were Cu_3Ge compound as judged from EDX data in Fig. 3(b) point A. Literature shows that the compound has low electrical resistivity [11]. Also, Ga has lower chemical potential in Cu_3Ge compound than in GaAs. This results in the out diffusion of Ga atoms from GaAs to the Pd layer and then to Cu_3Ge layer. Besides, Ge atoms also diffused into to the Pd layer as can be seen from point B of the EDX in Fig. 3(b). In addition, Fig 3(b) shows that there is no Cu atom diffusion into the GaAs substrate near the Pd/GaAs interface after 250 °C annealing for 30 sec. Additionally, the TEM images and EDX profiles of Pt/Ti/Pt/Cu/Cr ohmic structure after annealing at 310 °C are shown in Fig. 4. Fig. 4(a) shows the ohmic structure remains distinct layer by layer after annealing due to the good thermal stability of the material system. And Fig. 4 A to D show the EDX results of each ohmic metal layer. All the EDX data from different

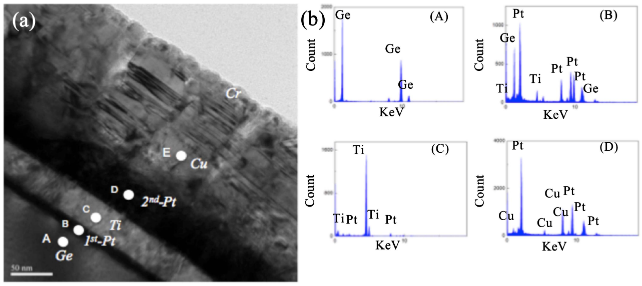

Fig. 4. The (a) cross sectional TEM image and (b) EDX analysis of p-Ge/Pt/Ti/Pt/Cu/Cr system.

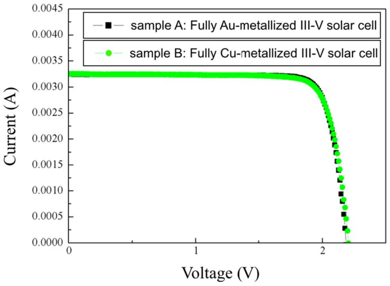

Fig. 5. The current-voltage (I-V) characteristics of InGaP/InGaAs/Ge triple-junction solar cells with Cu and Au metallization schemes measured at one-sun condition (AM 1.5, 25 °C).

TABLE I
THE CHARACTERISTIC PARAMETERS OF InGaP/InGaAs/Ge TRIPLE-JUNCTION SOLAR CELLS WITH DIFFERENT METALLIZATION SCHEMES MEASURED UNDER ONE SUN

Number	Area(cm^2)	V_{OC}(V)	I_{SC}(mA)	FF(%)	Effi(%)
Sample A	0.254	2.2	3.24	82.77	23.23
Sample B		2.21	3.22	82.48	23.11

areas A-D in Fig. 4(b) show no signal of Cu atom, meaning the Ti layer has effectively prevented Cu diffusion during the annealing process. In addition, from EXD data of point D, it can be seen that the Cu atoms diffused slightly into the second layer of Pt and Cu_3Pt formation was observed in the X-ray data.

Fig. 5 shows the I-V curves of the fully Cu-metallized InGaP/InGaAs/Ge solar cell and the conventional Au-metallized InGaP/InGaAs/Ge solar cell. The measured values of solar cell characteristic parameters for different metal schemes are listed in Table I. As evident from this table within measurement error, the efficiency for two devices are almost identical, under one sun measurement. The fill factors of these samples were about 82%. From the results shown above, the fully Cu-metallized InGaP/InGaAs/Ge solar cells demonstrates similar characteristics as conventional Au-metallized solar cells at one-sun condition (AM 1.5, 25 °C). Since the operation temperature of the concentrated solar cell systems is usually below 150 °C [12], we applied 250 °C thermal annealing to the Cu-metallized contacts and 150 °C thermal annealing to the fully Cu-metallized solar cells for 9 hours to study thermal stability. The results show that the contact resistance of Pd/Ge/Cu/5-μm Cu and Pt/Ti/Pt/Cu structures was still in the order of 10^{-6} Ω-cm^2 and the cell efficiency remained 23.11%.

IV. CONCLUSION

Au-free, fully Cu-metallized InGaP/InGaAs/Ge triple-junction solar cells using Pd/Ge/Cu as front contact and Pt/Ti/Pt/Cu/Cr as back contact and with Cu interconnects were fabricated and the results are reported for the first time. From the specific contact resistance measurements, these Cu-metallized ohmic contacts have low contact resistance in the order of 10^{-6} Ω-cm^2. XRD and TEM results clearly show the formation mechanisms of the Cu-metallization ohmic structures. For Pd/Ge/Cu contact, it was due to the Ge diffusion into the GaAs layer and the formation of Cu_3Ge compound, and for the Pt/Ti/Pt/Cu/Cr contact, it was due to high work function of Pt layer. These copper metallized contacts were quite stable even after 310 °C annealing. The I-V curves of the Cu-metallized InGaP/InGaAs/Ge triple-junction solar cells showed similar electrical characteristics (fig. 5) as the Au-metallized triple-junction solar cells. Overall, the Pd/Ge/Cu and Pt/Ti/Pt/Cu contacts and Cu based interconnects have been successfully applied to the InGaP/InGaAs/Ge triple-junction solar cells and demonstrated excellent electrical performance and thermal stability.

REFERENCES

[1] K. Nishiokaa *et al.*, “Evaluation of InGaP/InGaAs/Ge triple-junction solar cell and optimization of solar cell’s structure focusing on series resistance for high-efficiency concentrator photovoltaic systems,” *Solar Energy Mater. Solar Cells*, vol. 90, no. 9, pp. 1308–1321, May 2006.

[2] J. W. Leema *et al.*, “Efficiency improvement of III–V GaAs solar cells using biomimetic TiO_2 subwavelength structures with wide-angle and broadband antireflection properties,” *Solar Energy Mater. Solar Cells*, vol. 127, pp. 43–49, Aug. 2014.

[3] D. C. Lawa *et al.*, “Future technology pathways of terrestrial III–V multijunction solar cells for concentrator photovoltaic systems,” *Solar Energy Mater. Solar Cells*, vol. 94, no. 8, pp. 1314–1318, Aug. 2010.

[4] H. W. Yu *et al.*, “Effect of graded-temperature arsenic prelayer on quality of GaAs on Ge/Si substrates by metalorganic vapor phase epitaxy,” *Appl. Phys. Lett.*, vol. 99, no. 17, pp. 171908-1–171908-3, Oct. 2011.

[5] A. G. Baca *et al.*, “A survey of ohmic contacts to III–V compound semiconductors,” *Thin Solid Films*, vols. 308–309, pp. 599–606, Oct. 1997.

[6] S. Oktyabrsky *et al.*, “Cu_3Ge ohmic contacts to n-type GaAs,” *J. Electron. Mater.*, vol. 25, no. 11, pp. 1662–1672, Nov. 1996.

[7] E. D. Marshall *et al.*, “Nonalloyed ohmic contacts to *n*-GaAs by solid-phase epitaxy of Ge,” *J. Appl. Phys.*, vol. 62, no. 3, pp. 942–947, Mar. 1987.

[8] I. Rey-Stolle, B. Galiana, and C. Algora, “Assessment of a low-cost gold-free metallization for III–V high concentrator solar cells,” *Solar Energy Mater. Solar Cells*, vol. 91, no. 9, pp. 847–850, May 2007.

[9] K. A. Darling *et al.*, “Thermal stability, mechanical and electrical properties of nanocrystalline Cu_3Ge,” *Intermetallics*, vol. 16, no. 3, pp. 378–383, Feb. 2008.

[10] W. Macherzyński *et al.*, “Fabrication of ohmic contact based on platinum to p-type compositionally graded AlGaAs layers,” *J. Phys., Conf. Ser.*, 2009, vol. 146, no. 1, p. 012034.

[11] S. Oktyabrsky, M. O. Aboelfotoh, and J. Narayan, “Microstructure and chemistry of Cu-Ge ohmic contact layers to GaAs,” *J. Electron. Mater.*, vol. 25, no. 11, pp. 1673–1683, Nov. 1996.

[12] X. Ju *et al.*, “An improved temperature estimation method for solar cells operating at high concentrations,” *Solar Energy*, vol. 93, pp. 80–89, Jul. 2013.