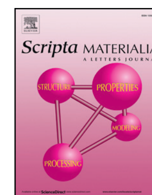
Scripta Materialia 152 (2018) 36–39

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat



Regular article

# Stable and low contact resistance electrical contacts for high temperature SiGe thermoelectric generators

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ARTICLE INFO

*Article history:*
Received 16 January 2018
Received in revised form 12 March 2018
Accepted 27 March 2018
Available online xxxx

*Keywords:*
Thermoelectric materials
Sputtering
Annealing
Refractory metals
Electrical contacts

ABSTRACT

The thermal stability and contact resistance of TaAlN thin films as electrical contacts to SiGe thermoelectric elements are reported. We demonstrate that a sharp interface is maintained after the device annealed at 800 °C for over 100 h, indicating that no interdiffusion takes place between TaAlN and SiGe. A specific contact resistivity of $(2.1 \pm 1.3) \times 10^{-6}$ Ω-cm$^2$ for p-type SiGe and $(2.8 \pm 1.6) \times 10^{-5}$ Ω-cm$^2$ for n-type SiGe is demonstrated after the high temperature annealing. These results show that TaAlN is a promising contact material for high temperature thermoelectrics such as SiGe.

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SiGe is a well-known high temperature thermoelectric material for which the thermoelectric figure of merit of p-type and n-type SiGe peaks at approximately 800 °C [1,2]. In order to achieve high device performance, it is important to find an electrical contact material that can survive such high temperatures with low resistivity, good adhesion to SiGe and low contact resistance. When considering the selection of contact materials, most pure metals can be ruled out because of their tendency to oxidize. Conducting oxides such as $RuO_2$ are potential candidates [3,4] but the formation of gaseous $RuO_3$ and $RuO_4$, as well as the tendency of $RuO_2$ to decompose to Ru at elevated temperatures makes the oxide unstable. In addition, the cost of Ru is high [5,6]. Sputtered Ta-N films were reported to have high electrical conductivity [7], however they are easily oxidized in the temperature range of 250–500 °C [8]. $Si_3N_4$ has been added to TaN to improve its thermal stability [7,9,10]. The ternary systems (Ta, W)-Si-N have been well studied as contact and interconnection materials in silicon based integrated circuits [7,9]. Both ternary compounds failed stability tests after annealing at 900 °C for 30 min [11]. The system of $TiB_2 + Si_3N_4$ was reported as a diffusion barrier to p-type SiGe [10,12], with the specific contact resistivity (SCR) being $7.5 \times 10^{-5}$ Ω cm$^2$ after aging at 1000 °C for 120 h [12], However, those samples were encapsulated in vacuum in quartz tubes during the annealing. The application was a radioisotope thermoelectric generator to be used in outer space [12]. This kind of vacuum packaging greatly increases the cost of the thermoelectric generators. Here, we investigated AlN as a replacement for $Si_3N_4$ and studied the TaAlN ternary thin film as an electrical contact to SiGe at high temperature. The low cost of the constituent materials, tunable work function, metallic behavior, and good stability at elevated temperatures makes it an ideal candidate for SiGe thermoelectric applications [6,13,14].

Magnetron sputter deposition was used to prepare both the SiGe and TaAlN films. The composition and doping level of the thin-film SiGe were selected to match those of bulk SiGe, which is commonly used for thermoelectric applications. SiGe films were deposited onto 500 nm $Si_3N_4$/Si (100) substrates using co-sputtering from Si and Ge targets. The films were annealed in a tube furnace at 1000 °C in $N_2$ for 1 h to form polycrystalline SiGe (Fig. S1). This process is similar to previously reported processes in the literature [15]. Boron was then introduced into the films using a thermal diffusion process [16]. In comparison, the deposition of TaAlN films was done using DC reactive magnetron sputtering using Ta and Al targets with a mixed carrier gas of $Ar/N_2$. The thickness of the as-deposited TaAlN films was approximately 340 nm, measured using cross-sectional scanning electron microscopy (SEM). For RBS analysis, films with a thickness of approximately 85 nm of TaAlN were prepared on SiGe/$Si_3N_4$/Si substrates. The RBS experiments were carried out using a KOBE HRBS-

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https://doi.org/10.1016/j.scriptamat.2018.03.040
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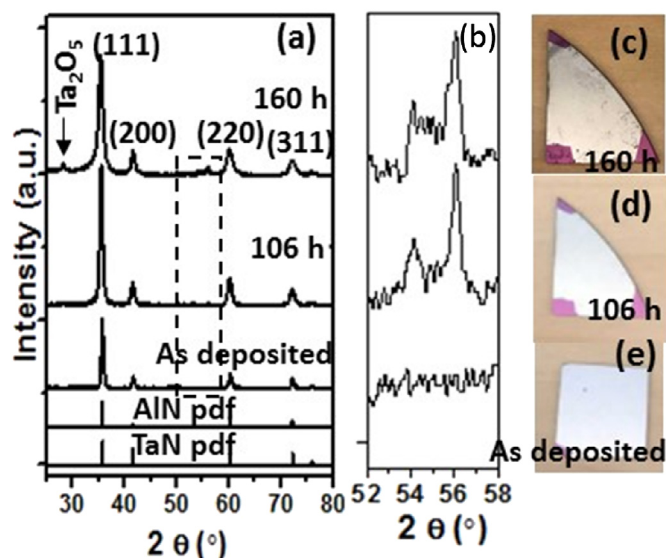


**Fig. 1.** XRD patterns for (a) as-deposited and post-annealed $Ta_{0.33}Al_{0.11}N_{0.56}$ films on $Si_3N_4$/Si substrates: the films were annealed for 106 h and 160 h at 800 °C in $N_2$. (b) Expansion of the region between 2θ = 52° and 58° as marked with a dashed line in (a). Results in the literature suggest this peak could be $Al_5O_6N$ [20]. Photos for: (c) 160 h at 800 °C, (d) 106 h annealed sample at 800 °C, and (e) as-deposited sample.

V500 system located in the Imaging and Characterization Core Laboratory at KAUST. A detection angle of 107.5° and a 400 keV beam of $He^+$ ions were used for the analysis. The composition of the deposited SiGe was determined to be $Si_{0.74}Ge_{0.26}$ using RBS, while the boron doping concentration is $4 \times 10^{19}$ $cm^{-3}$, determined using Hall measurements [17]. The TLM method was used to obtain the SCR, the details of which can be found in earlier studies [18,19]. The bright field-scanning transmission electron microscopy (BF-STEM) imaging and energy dispersive X-ray spectroscopy (EDS) mapping images were obtained using a JEM-ARM 200F (JOEL, USA Inc.) operated at 200 kV [19]. To study the film interface, a cross-sectional TEM lamella was prepared using a focused ion beam (FEI Nova 200). Electron-beam assisted carbon deposition (approximately 200 nm) was performed onto the TaAlN film surface prior to the deposition of $SiO_2$ to prevent surface oxidation.

Several sputtering process parameters were studied to optimize the stability of the TaAlN films. These studies revealed that a Ta deposition power of 9.7 W/$cm^2$, Al deposition power of 4.9 W/$cm^2$ and a carrier gas combination of 16 sccm Ar/4 sccm $N_2$ give a film with good conductivity, low electrical contact resistance, and good thermal stability. These TaAlN films were post-annealed in a tube furnace in an $N_2$ ambient to carry out the thermal stability tests. Photos of 160 h and 106 h as well as the as-deposited TaAlN Samples post annealed at 800 °C are shown in Fig. 1c–e. No color change or signs of delamination are seen for the 106 h annealed film, consistent with good thermal stability. The films start to show delamination after 160 h at 800 °C. Fig. 1a shows the XRD spectra for as-deposited, 106 h and 160 h annealed films. Overall, the film maintains the same TaAlN phase after post-deposition annealing. New diffraction peaks are observed at 56.03° and at 28.23° after annealing at 800 °C for 106 h and 160 h, respectively. Because the intensities of these peaks are weak, it is difficult to conclusively assign them to any specific phases. Results in the literature suggest these peaks could be $Al_5O_6N$ (56.03°) and $Ta_2O_5$ (28.23°) [20,21]. Because the diffraction peaks of AlN and TaN show up at similar diffraction angles, it is difficult to assign the peaks to either component (Fig. 1a). There are no diffraction peaks observed for elemental Al or Ta, indicating that complete reaction within the sensitivity of XRD of Al and Ta with $N_2$ has taken place. Complete reaction is further supported by XPS surface and depth profiling analysis, where no metallic Ta or Al species are observed (Fig. S2) [22,23].

We also investigated the electrical resistivity of the TaAlN films. According to Bjørk's study, in order to maintain >95% thermoelectric device efficiency, the electrical contact resistance needs to be <10% of the total leg resistance [24]. The electrical contact resistance consists of the resistance of the contact electrode and the contact resistance between the electrodes and TE material. For bulk SiGe with dimensions of 5 × 5 × 15 mm [3,10], the resistance of the total leg of SiGe is approximately 0.018 Ω [1]. Therefore, the contact resistance at one side needs to be $<9 \times 10^{-4}$ Ω in order to maintain 95% device efficiency. The measured resistivity of the as-deposited TaAlN film is $(3.8 \pm 0.6) \times 10^{-4}$ Ω-cm, as determined by 4-point probe measurement. For example, if we use a contact metal with a thickness of 1 μm, according to R = ρL / A, where R is the resistance of the film, ρ is film resistivity, L is thickness of the material and A is the cross-sectional area, the resistance of the as-deposited TaAlN film on one end of the thermoelectric leg is calculated to be $2 \times 10^{-7}$ Ω, which is much less than the required contact resistance. Therefore, the resistance of the as-deposited TaAlN electrodes can be neglected. The post-annealing effect on electrical resistivity is shown in Fig. 2a, where the resistivity of the film increases with increasing post-annealing time. The resistivity increases 50% in the first 19 h, which is likely due to surface oxidation of the film. The resistivity then slowly increases to $(5.2 \pm 0.2) \times 10^{-4}$ Ω-cm after 73 h of annealing, indicating no significant film quality change. The resistivity increases to $(6.5 \pm 0.2) \times 10^{-4}$ Ω-cm after annealing at 800 °C for 106 h. Even after 106 h of annealing, the resistance of TaAlN is still low enough to be neglected.

Since the resistance of the contact metal is small enough to be neglected, the SCR needs to be $<7.2 \times 10^{-5}$ Ω-$cm^2$ in order to achieve device efficiency >95%. Fig. 2b summarizes the SCR change of the

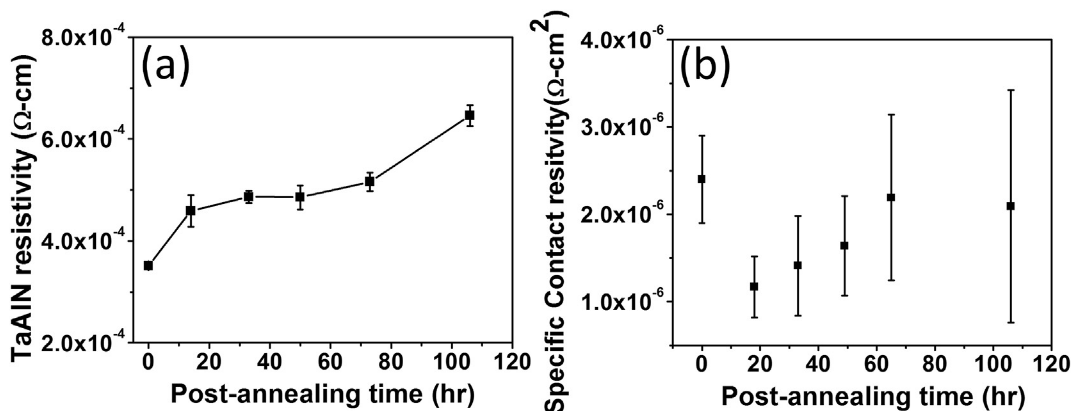


**Fig. 2.** (a) $Ta_{0.33}Al_{0.11}N_{0.56}$ film resistivity as a function of post-annealing time at 800 °C. The TaAlN films were deposited on $Si_3N_4$/Si substrates with a thickness of 340 nm. (b) SCR values of TaAlN/p-$Si_{0.74}Ge_{0.26}$ contacts as a function of post-annealing time.

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