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Graphical abstract

a) Specific contact resistivity for Ni/Mg₂Si contacts.

Cross-sectional STEM images of Ni/Mg₂Si films: b) as deposited; c) after annealing at 400 $^{\circ}\text{C}$ for two hours; d) after annealing at 450 $^{\circ}\text{C}$ for two hours.

Contact resistance and stability study for Au, Ti, Hf and Ni contacts on thin-film Mg₂Si

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Abstract: We present a detailed study of post-deposition annealing effects on contact resistance of Au, Ti, Hf and Ni electrodes on Mg₂Si thin films. Thin-film Mg₂Si and metal contacts were deposited using magnetron sputtering. Various post-annealing temperatures were studied to determine the thermal stability of each contact metal. The specific contact resistivity (SCR) was determined using the Cross Bridge Kelvin Resistor (CBKR) method. Ni contacts exhibits the best thermal stability, maintaining stability up to 400 °C, with a SCR of approximately 10⁻² Ω-cm² after annealing. The increased SCR after high temperature annealing is correlated with the formation of a Mg-Si-Ni mixture identified by cross-sectional scanning transmission electron microscopy (STEM) characterization, X-ray diffraction characterization (XRD) and other elemental analyses. The formation of this Mg-Si-Ni mixture is attributed to Ni diffusion and its reaction with the Mg₂Si film.

Keywords: Thermoelectric, thin-film Mg_2Si , specific contact resistivity (SCR), cross bridge kelvin resistor (CBKR) method, Ni diffusion, stability

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1. Introduction:

Thermoelectric generators (TEG) can be used to transform waste heat into electricity. Because of the high reliability and quiet operation, thermoelectric generators have widespread applications in the electronics and automotive industries [1]. When mainly considering the electrical factors, the performance of a thermoelectric generator is determined by the thermoelectric figure-of-merit ZT , where T is the absolute temperature, and ZT is the device figure-of-merit, namely [2],

$$ZT = zT \left(\frac{L}{L + 2\rho_c \sigma} \right) \quad [1]$$

where L is the device leg length, ρ_c is the specific contact resistivity, σ is the bulk material electrical conductivity, and zT is the material figure-of-merit.

$$zT = \frac{\sigma S^2}{\kappa} \quad [2]$$

where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity. As seen in Equation 1, ρ_c limits Z significantly as L is reduced. Therefore, device performance can be greatly improved by reducing the contact resistivity when the devices are scaled down, especially when $L < 100 \mu\text{m}$ [2].

Mg_2Si was chosen as the thermoelectric material due to its potential low cost, its low density, high natural abundance of the constituent materials, and environmentally friendly nature [3–8]. Most research on Mg_2Si has focused on developing Mg_2Si with high zT [3–8], while only a few papers investigated the contact resistance, based on bulk Mg_2Si [9–12]. Since the contact resistance is a surface phenomenon, a direct study of SCR on thin-film Mg_2Si is desired.

In this study, we used a cross bridge kelvin resistor (CBKR) method to evaluate the contact resistance for sputtered thin-film Mg_2Si . The CBKR method has a high sensitivity, 10^{-10}

$\Omega\text{-cm}^2$, when used in thin film studies [15, 16]. Compared with SCR studies of bulk materials [9-14], the CBKR method has the following three advantages: 1) the contact area is well defined in the thin film CBKR pattern, which is difficult with bulk materials, due to the contact sintering process; 2) the oxidation of the sample surface is removed using Ar^+ ion sputtering prior to metal deposition, which provides a better indication of the true contact resistance [2], and 3) room temperature deposited contacts are accessible for measurements since high temperature annealing is not necessary for the contact formation. Metal contacts using Au, Ti, Ni and Hf were examined after elevated temperature annealing. These experiments provide accurate determination of SCR for the contact metal systems on Mg_2Si .

2. Experimental Methods

2.1 Sample Preparation

A Mg_2Si compound target (99.9%, Angstrom Sciences) was used for the sputter-deposition of the thin-film Mg_2Si . The deposition process was carried out when the base pressure in the chamber reached 10^{-8} Torr. The thin-film Mg_2Si samples were deposited using an RF power density of 3.7 W/cm^2 , an Ar flow rate of 20 sccm, a deposition time of 100 min, and a substrate temperature of 200°C . The thickness of the deposited Mg_2Si film is approximately 200 nm, determined using a Veeco Dektak VIII Profilometer. Four-inch $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ ((100), P-doped) wafers were used as substrates, where a 500 nm Si_3N_4 layer was deposited using Low-Pressure Chemical Vapor Deposition (LPCVD) on top of a 500 nm thermally grown SiO_2 layer.

To evaluate the SCR, a mesa structure (Fig. 1) was fabricated using a two-mask optical-lithography process. S1813 photoresist was spin-coated on top of the Mg_2Si , followed by optical patterning and wet-etching. The etchant for Mg_2Si was Buffered Oxide Etch (BOE 7:1). The

contact metal layer was patterned using a lift-off process. Before depositing the metal contacts, the Mg_2Si surface were pre-sputtered using Ar^+ at 10 mTorr pressure and 50 W power to remove the surface oxide, as well as other contaminants. The contact metal (Au, Hf, Ti or Ni) was sputtered onto the patterned Mg_2Si thin film to a thickness of approximately 300 nm. For the Hf, Ti and Ni metal contacts another 100 nm Au layer was deposited on top in order to prevent oxidation of the contact metal when exposed to air. The post-annealing experiments were conducted at 100°C and 200 °C for two hours on a hot plate in a N_2 filled glove box. For higher annealing temperatures of 300 °C, 400 °C and 450 °C, the post-annealing experiments were conducted in a MiniBrute furnace with flowing forming gas (95% N_2 , 5% H_2) at a flow rate of 4 L/min for two hours.

2.2 CBKR Method

The CBKR measurements were carried out using a Cascade Summit probe station equipped with an LR2000 Milliohmmeter (QuadTech, Inc.).

The mesa structure shown in Fig. 1 (a) was used for the CBKR measurements. The regions marked with a cross are the metal-semiconductor contact pads. The CBKR measurement was conducted by measuring the voltage between pads 1 and 2 while applying current through pads 3 and 4. The contact pad size is designed to be $25 \times 25 \mu\text{m}$ in order to place 2 electrical probes on the same pad simultaneously. Because of the high conductivity of the metal contacts, the resistance of the metal itself was neglected. The contact resistance R_c can be obtained directly if there is a perfect alignment between the metal pad and the patterned semiconductor using Equation 3 [17].

$$R_C = \frac{V_{12}}{I_{34}} = \frac{\rho_c}{A_c} \quad [3]$$

where V_{12} is the voltage between pads 1 and 2 and I_{34} is the current flow between pads 3 and 4. A_c is the contact area and ρ_c is the SCR. The SCR can be extracted by multiplying R_C by the contact area A_c . For patterns with some misalignment, the corrected contact resistance can be determined using CBKR by using Equation 4 [17]:

$$R_C = \frac{\rho_c}{A_c} + \frac{4R_s\delta^2}{3W_xW_y} \left[1 + \frac{\delta}{2(W_x - \delta)} \right] \quad [4]$$

where R_s is the sheet resistance of the semiconductor, W_x and W_y are the width of the Mg_2Si pattern shown in Fig. 1 (b), δ is the misalignment shown in Fig. 1 (c). When $\delta \neq 0$, there is an additional voltage drop at the contact periphery, which is known as the lateral current crowding effect [18]. It leads to an apparent difference between measured and actual values of ρ_c . To eliminate or reduce the error, δ needs to be 0 or close to 0. A 7×7 matrix of CBKR patterns was designed to achieve minimal misalignment for at least one pattern, as previously proposed by Isogai et al. [19], shown in Fig. 1 (d). The built in misalignment in both the x, y directions is designed to be -1.5, -1, -0.5, 0, 0.5, 1 and 1.5 μm . In Fig. 1 (d), the upper left corner is set as the reference point (0, 0), indicated with the cross hair. However, Equation 4 only covers the situation where the misalignment is same in both x and y directions, and the metal contact pads are smaller than the corner area, see Fig.1 (b). Whereas in the real practice, the metal contact can be larger than the corner area with unequal misalignment in x and y directions, see supplementary Fig. 2. Therefore the misalignment correction of the measured SCR was done through numerical simulation method using COMSOL Multiphysics software, the simulation process and an example is described in the supplementary section (Supplementary Fig.1, 2). The results are shown in Table 1 [20].

2.3 Material Characterizations

The microstructure of the thin-film Mg_2Si with metal contacts was characterized using STEM. X-ray diffraction measurements (XRD, Rigaku Ultima III) were performed to determine the crystal phase of the thin-film Mg_2Si and the mixture formed due to Ni diffusion after annealing.

The cross-sectional lamellas for TEM analysis were prepared using a FEI Nova 200 NanoLab DualBeam focused ion beam scanning electron microscope (FIB-SEM). A thin layer of electron beam assisted SiO_2 was deposited prior to the routine ion beam assisted Pt protection layer in order to provide better image contrast for TEM analysis and to protect the sample surface from ion beam damage during the FIB milling process. A Ga^+ ion beam current of 5 nA at 30 kV was used for the trench mill. Then the small lamella ($\sim 1\mu\text{m}$ in thickness) was transferred to an Omniprobe Lift-out grid for further thinning using an In-Situ Lift-Out technique [21]. A Ga^+ ion beam of 100 pA at 30 kV was used for thinning down the lamella until electron transparency (~ 100 nm), followed by the final polishing using a Ga^+ ion beam current of 20 pA at 5 kV.

To study the 3D microstructure of nickel diffusion into Mg_2Si thin films, slice-and-view was performed using a FEI Nova 200 Nano dual beam system. An E-beam assisted Pt protection layer was deposited prior to the slice-and-view analysis to improve the image quality and reduce the charging effect.

A Ga^+ ion beam of 1 nA at 30 kV was used to slice the sample. The SEM images were acquired using a back scattered electron (BSE) detector. A total of 84 slices were analyzed with the thickness of each slice being about 8 nm, so the volume of material analyzed by the slice and

view study was $2.4 \times 0.3 \times 1.5 \text{ } \mu\text{m}^3$ in size. The images were initially aligned using ImageJ software [22, 23]. The image segmentation, 3D reconstruction, volume rendering and visualization was carried out using Avizo Fire software (VSG Co., USA).

High resolution transmission electron microscopy (HRTEM) and energy filtered transmission electron microscopy (EFTEM) were performed with a JEOL JEM2100F microscope equipped with a Gatan Imaging Filter (GIF-Tridem, 2000×2000 CCD) operated at 200 kV. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and Energy dispersive X-ray spectroscopy (EDX) line scans were performed with a JEOL ARM200F microscope operated at 200 kV with a probe aberration corrector to study the chemical information at the Ni/Mg₂Si interface. To study the chemical distribution at the Ni/Mg₂Si interface, Energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) line scans have been performed. The collection semi-angle for EELS is 30 mrad with 1 eV energy resolution and the acquisition time is 2s/pixel.

3. Results and discussion

Fig. 2 shows the XRD spectrum of a Mg₂Si thin film prior to metal deposition. In addition to the majority Mg₂Si phase, a Mg phase is also observed, as evidenced by the peaks at 36.59° , 34.27° and 32.15° . In previous studies from Le-Quoc et al. [24, 25], excess Mg is also observed in Mg₂Si films prepared by sputtering. It is difficult to control the exact stoichiometry using sputtering due to different sputtering rates of different elements when using multiple sputtering targets. When using a Mg₂Si target, extra Mg is usually added (~3%) to compensate the loss of Mg due to the high vapor pressure and low condensation rate of Mg [26, 27]. We conducted our CBKR measurements using these sputtered Mg₂Si films.

For this study we chose four different contact metals to evaluate the SCR to Mg_2Si . Hf and Ti were selected due to their similar work function [28–30] and thermal expansion coefficient [10] to Mg_2Si (Table 1). Ni was selected because it has shown promising results with low contact resistance during high temperature annealing in previous bulk Mg_2Si studies [9–11]. A 100 nm Au layer is sputtered onto the metal contacts to protect them from surface oxidation and contamination. Au was selected as the fourth contact metal to provide a reference for a noble metal.

In order to avoid film oxidation, post-annealings under low temperatures (100°C and 200°C) were performed in glovebox filled with N_2 (O_2 and $\text{H}_2\text{O} < 5$ ppm). Due to the limit of high temperature allowed in the glovebox, high temperature post-annealings (300°C and 400°C) were carried out in a forming gas (FG, 95% N_2 and 5% H_2) environment in a THERMCO Minibute furnace. The resistivity of the thin film Mg_2Si samples was obtained using transfer line measurement [2], see Supplementary Table 4.

Sample processing conditions and SCR results are summarized in Table 2. The SCR of Au is approximately 10 times higher than that of the other three metals. Devices with Hf, Ti, and Ni contacts show low SCR of approximately $10^{-4} \mu\Omega\text{-cm}^2$ for as-deposited films.

The different SCR values can be understood by the formation of different types of electrical contacts. According to the Schottky-Mott rule [31], since Mg_2Si is a low work function n-type semiconductor (Table 1), it is expected to form an Ohmic contact and exhibit low SCR values with low work function metals such as Hf and Ti. Conversely, it is expected to form a Schottky contact and exhibit high SCR values with high work function metals such as Ni and Au. We note that all of the metals tested, except for Ni, follow this rule. Since Ni is more reactive

than Au, it is possible to form a large number of interfacial electronic states at Ni-Mg₂Si interface, which could alter the band-alignment between Ni and Mg₂Si, and facilitate the charge transfer between TE materials and the metal contact. A more detailed understanding on the interfacial composition and electronic states is required to understand the low SCR value of Ni/Mg₂Si contact in the future.

Because Ti, Ni and Hf contacts showed promising SCR results, we explored the effect of post-deposition annealing conditions for these three contacts to determine their thermal stability. As seen in Table 2, when the annealing temperature increases to 300°C, the SCR for Hf/Mg₂Si, Ti/Mg₂Si and Ni/Mg₂Si contacts changes to 1.8×10^{-3} (as deposited 2.9×10^{-4}), 9.8×10^{-4} (as deposited 1.2×10^{-3}), and 2.4×10^{-3} (as deposited 2.1×10^{-4}) $\Omega\text{-cm}^2$ respectively. When the annealing temperature increases to 400°C, a color change for the Ti and Hf electrodes was observed, while no change is observed in the Ni contact pad color. (Supplementary Fig. 4) Ni/Mg₂Si contacts were also annealed at 400 °C for 24 hours, with the obtained SCR equal to 1.5×10^{-2} $\Omega\text{-cm}^2$. Higher temperature annealing with Ni electrodes at 450 °C caused a pad color change as well. Such color change indicates the degradation of the contacts. Fig. 3 shows the SCR results of Ni/Mg₂Si contacts with different post-annealing conditions. The obtained specific contact resistivity are higher than the values from Thimont ($5.5 \pm 0.3 \mu\Omega\text{-cm}^2$) et al. [9] and de Boor et al. ($4.4 \pm 2.7 \mu\Omega\text{-cm}^2$) [11, 12] using a sintering process for their Ni-Mg₂Si contact. The noticeable difference is they investigated doped bulk Mg₂Si and used a different synthesis technique. During the sintering process, Ni will react with the bulk Mg₂Si to form a thick interfacial layer (20-30 μm [11, 12]); this interfacial layer includes multiple phases. Here we sputter the Ni contact onto Mg₂Si films, resulting in a distinct Ni-Mg₂Si interface. Furthermore, non-intentionally doped thin-film Mg₂Si films were used for contact study, which has a higher

sheet resistance than the doped bulk Mg_2Si [10]. In the literature, the studied interfaces were new phases generated during sintering to doped Mg_2Si ; in our case, it is Ni contacts to non-intentionally doped Mg_2Si . The composition at the interface is different, and therefore the results are not comparable. The contact resistance study from de Boor and Thimont are important for bulk Mg_2Si contact fabrication, while the sputtered contact study in this paper can provide useful information of room temperature deposited contacts as well as the limits for the intrinsic contact resistance, especially after high temperature annealing.

Since the SCR value for the Ni contacts stay constant up to a higher temperature than Hf and Ti, we investigated the chemistry and the microstructure of the Ni/ Mg_2Si interface after high temperature annealing to understand the change in SCR. Cross-sectional studies on Ni/ Mg_2Si interfaces were conducted using STEM, electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDS). As expected, a sharp Ni/ Mg_2Si interface is observed prior to thermal annealing (Fig. 4 (a)), with no sign of chemical reaction or interdiffusion (See Supplementary Fig. 5 (b)). After annealing at 400°C for two hours, a diffused region is observed, which is distinct from both Ni and Mg_2Si (Fig. 4 (b)). After annealing at 450°C in forming gas for two hours, the size of the diffused region increases (Fig. 4 (c)). According to EELS and EDS analyses, the features labeled Ni and Mg_2Si in the STEM images are confirmed to be pure Ni and pure Mg_2Si , respectively, whereas the feature labeled as Ni diffusion is composed of all three elements (Mg, Ni, and Si). Therefore, we attribute this diffused feature to a mixture of Ni and Mg_2Si resulting from Ni in-diffusion.

EELS mapping and focused ion beam tomography provided valuable insight into the formation of the Mg-Si-Ni mixture. Fig. 5 (b), (c) and (d) show the elemental mapping of Si, Ni, and Mg for the corresponding TEM image (Fig. 5 (a)). It shows that the Mg-Si-Ni mixture can

form islands near the $\text{Mg}_2\text{Si}/\text{Si}_3\text{N}_4$ contact, without apparent connections to the Ni electrode. The 3-D tomography constructed using focused ion beam slice-and-view (Fig. 5 (e), (f), (g)) reveals an interpenetrating morphology between the Ni-rich phase and the Mg_2Si phase, clearly showing that the islands near the $\text{Mg}_2\text{Si}/\text{Si}_3\text{N}_4$ interface are laterally connected to the Ni-rich phase. A 3-D video is also shown in the Supplementary section (Supplementary Video 1). Based on these results, we assume that the formation of Mg-Si-Ni mixture originates from Ni diffusion and reaction along the grain boundaries of the Mg_2Si thin films. Otherwise, a uniform gradient of Ni concentration is expected from the Ni/ Mg_2Si interface to the $\text{Si}_3\text{N}_4/\text{Mg}_2\text{Si}$ interface, which is clearly not the case in our observation.

Grazing angle XRD characterization was performed on the post-annealed Ni/ Mg_2Si samples (Fig. 6). Before thermal annealing, the Ni/ Mg_2Si stack shows only Mg_2Si , Mg and Ni peaks, consistent with the TEM results that showed no mixed phase. After high annealing temperatures, a new set of diffraction peaks appear in the XRD spectrum, which do not match any existing material in the powder diffraction file (PDF) database. According to EELS and EDS results, we tentatively assign these peaks to the formation of a mixture of Mg-Si-Ni (Fig. 6, squares). While the exact stoichiometry of the Mg-Si-Ni mixture cannot be determined from current results, it is noteworthy that both $\text{Mg}_6\text{Si}_7\text{Ni}_{16}$ and Mg_2SiNi_3 are thermodynamically stable compounds according to first-principle calculations, with formation energies of -0.548 eV and -0.47 eV, respectively [32, 33]. Further experimental characterization and theoretical investigation are needed to provide additional information about this Mg-Si-Ni mixture phase.

4. Conclusions

In conclusion, the CBKR method is applied to evaluate the SCR of thin film Mg_2Si with Au, Ti, Hf and Ni contacts. The Ni contact is particularly promising as it remains stable with a low SCR ($10^{-2} \Omega\text{-cm}^2$) to higher annealing temperature (400°C). Higher temperature annealing treatment increases the SCR, which is due to the formation of a mixture of Mg-Si-Ni. This study reveals the importance of contact optimization for high performance and stable thermoelectric devices, especially if they are to be operated at elevated temperatures.

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Figure caption

Fig. 1. (a) An example of the CBKR pattern. (b) W_x and W_y represent the width of the Mg_2Si pattern, L_x and L_y represent the width of the contact pad. (c) The (0, 0) point is marked with a cross. The misalignment was measured based on this point. (d) A schematic of the CBKR matrix. The mesa structure in the center is the pattern with perfect alignment. Others are misaligned with a pre-determined misalignment [19].

Fig. 2. XRD pattern of thin-film Mg_2Si deposited using magnetron sputtering at a deposition temperature of 200 °C.

Fig. 3. Summary of SCR results for Ni/ Mg_2Si contact with different post processing conditions. 100, 200, 300 and 400 represents the annealing temperature. N2 means the anneals were done in glovebox filled with N_2 . FG means the anneals were done in a forming gas (FG, 95% N_2 and 5% H_2) environment in a THERMCO Minibrute furnace. Ni_400_FG_24 represents the Ni/ Mg_2Si contacts were annealed in forming gas at 400°C for 24 hr. The annealing time for all the other anneals were two hours.

Fig. 4. Cross-sectional STEM images of Ni/ Mg_2Si films; (a) as-deposited, (b) after annealing at 400 °C for two hours, (c) after annealing at 450 °C for two hours. (d) EELS line scan, and (e) EDS line scan across the Ni/ Mg_2Si sample after 2hr 450 °C forming gas anneal along the red arrow shown in (c).

Fig. 5. (a) Zero loss image for Ni/ Mg_2Si films for EELS mapping, and (b), (c), (d) the EELS mapping of (b) Si, (c) Ni and (d) Mg, of the Ni/ Mg_2Si films annealed at 400°C for two hours.

Brighter features indicate a higher density of the corresponding element. (e), (f) focused ion beam slice-and-view tomography for (e) the Ni-rich phase obtained using Slice and View and processed using ImageJ and Avizo Fire software, i.e. both the Ni electrode and the Mg-Si-Ni mixture, which are not distinguishable in the FIB images, and (f) the Mg₂Si phase.

Fig. 6. XRD patterns of Mg₂Si with as-deposited Ni electrode (magenta), after 400°C post annealing for 2 hours (green), and after 450°C post annealing for 2 hours (dark blue).

Fig. 1. (a) An example of the CBKR pattern. (b) W_x and W_y represent the width of the Mg_2Si pattern, L_x and L_y represent the width of the contact pad. (c) The $(0, 0)$ point is marked with a cross. The misalignment was measured based on this point. (d) A schematic of the CBKR matrix. The mesa structure in the center is the pattern with perfect alignment. Others are misaligned with a pre-determined misalignment [19].

Fig. 2. XRD pattern of thin-film Mg_2Si deposited using magnetron sputtering at a deposition temperature of 200 $^{\circ}\text{C}$.

Fig. 3. Summary of SCR results for Ni/Mg₂Si contact with different post processing conditions. 100, 200, 300 and 400 represents the annealing temperature. N2 means the anneals were done in glovebox filled with N₂. FG means the anneals were done in a forming gas (FG, 95% N₂ and 5% H₂) environment in a THERMCO Minibrute furnace. Ni_400_FG_24 represents the Ni/Mg₂Si contacts were annealed in forming gas at 400°C for 24 hr. The annealing time for all the other anneals were two hours.

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Table 1 Properties of Mg₂Si and contact metals

Material	Work function (eV) ^a	Linear Thermal expansion coefficient (10 ⁻⁶ K ⁻¹) ^b
Mg ₂ Si	3.59	7.5
Ti	4.33	8.4-8.6
Ni	5.15	13
Hf	3.9	6.1
Au	5.1	14.2

a. Work functions for each material were taken from Ref 10 [Mg₂Si], Ref 28 [Ti, Hf, Au], and Ref 29, 30 [Ni]. b. Linear thermal expansion coefficients were taken from Ref 11.

Table 2. Summary of sample processing conditions and the corresponding SCR.

Sample identification	Contact metal	Post annealing condition (°C)	Post annealing time (hours)	SCR after misalignment correction ($\Omega\text{-cm}^2$)
Ni_none	Ni	N/A	0	$(2.1 \pm 0.5) \times 10^{-4}$
Ni_100_N2	Ni	100	2	$(8.6 \pm 1.5) \times 10^{-4}$
Ni_200_N2	Ni	200	2	$(4.5 \pm 0.9) \times 10^{-3}$
Ni_300_FG	Ni	300	2	$(2.4 \pm 0.6) \times 10^{-3}$
Ni_400_FG	Ni	400	2	$(4.3 \pm 2.8) \times 10^{-2}$
Ni_400_FG_24	Ni	400	24	$(1.5 \pm 0.7) \times 10^{-2}$
Hf_none	Hf	N/A	0	$(2.9 \pm 1.4) \times 10^{-4}$
Hf_300_FG	Hf	300	2	$(1.8 \pm 0.6) \times 10^{-3}$
Ti_none	Ti	N/A	0	$(1.2 \pm 0.4) \times 10^{-3}$
Ti_300_FG	Ti	300	2	$(9.8 \pm 4.5) \times 10^{-4}$
Au_none	Au	N/A	0	$(1.5 \pm 0.3) \times 10^{-3}$
Au_100_N2	Au	100	2	$(3.0 \pm 1.4) \times 10^{-3}$

Supplementary Information:

COMSOL simulation

The error in measured specific contact resistivity (SCR) caused by the misalignment between metal pad and the underneath mesa corner is corrected by numerical simulation using COMSOL software [1], which uses a finite element method to solve the Continuity equation [2]. The geometry of the CBKR device is built in COMSOL using the measured dimensions. A small current (1 or 0.1 μA) is set to flow from pad 2 to pad 1. The top surface of pad 1 is set as electrical ground, see Figure 1(a). The calculated electrical potential on pad 3 is used to extract the expected contact resistance value. The value of SCR used as an input to the simulation is swept over a certain range until the extracted contact resistance value becomes the same, or close, to the measured contact resistance value. This selection process is relatively simple because the extracted contact resistance always increase monotonically with the input SCR. The other main input values for the simulation are the conductivity (or resistivity) of the semiconductor mesa. When a Ni contact on top of the Mg_2Si is annealed at 400°C , an amount of Ni diffused into the Mg_2Si , reducing the resistivity. Experiments show the resistivity of Mg_2Si under Ni contact is approximately 50% of that of the rest of the Mg_2Si area. In simulation of the 400°C annealed sample, the resistivity of Mg_2Si under the Ni contact and the rest of Mg_2Si part are set to different values, as determined by experiments. However, since the resistivity change is very small, the difference in simulation results between uniform Mg_2Si resistivity vs varied Mg_2Si resistivity is small.

Figure 1. (a) Schematic diagram of CBKR geometry used in the COMSOL simulation. (b) A representative COMSOL simulation result shows the electrical potential distribution when $1\mu\text{A}$

is flowing from pad 2 to pad 1 when the SCR is set at $2 \times 10^{-7} \Omega \cdot \text{cm}^2$. The color legend shows the range of the electrical potential.

Sometimes the numerically corrected SCR is larger than the measured value. In CBKR, the voltage sensing arm is measuring the potential change over the metal-semiconductor interface which is averaged over the whole contact width, by default the voltage arm width, marked as “A” as shown in Figure 2. Sometimes the lithography misalignment causes the metal contact to be wider than voltage sensing arm, and the metal contact pads are extended toward the current flowing direction. When the semiconductor mesa has high resistivity compared to the contact resistivity, the current will flow into the metal pads at the front edge of the pad, see Figure 2(b). Since most current flows into metal pad before it reaches section A, the potential change in section A would be much smaller than the case when the current is uniformly distributed over the whole width of the metal-semiconductor interface, producing a much smaller SPC value. In this case, the simulation corrected value will be bigger than the measured value.

Figure 2. Schematic diagrams of examples for (a) planar view of CBKR device when the contact pad is larger than the voltage sensing arm. (b) Cross-sectional view of CBKR device and the current flow path (indicated by the red arrows) when the contact pad is larger than the voltage sensing arm.

An example using numerical simulation to determine the corrected specific contact resistivity value is shown below. This CBKR device is Ni contact on Mg_2Si (deposited 200°C), then annealed at 400°C .

The geometry of this cross-bridge kelvin resistor (CBKR) device is determined by SEM, as shown in Table 1:

Table 1: Measured contact resistance and dimensions for the CBKR pattern for the simulation correction in the example

R_{measured} (Ω)	SCR ($\Omega \cdot \text{cm}^2$) as measured	D_x (main) (μm)	D_y (main) (μm)	D_x (up) (μm)	D_y (up) (μm)	W_x (μm)	W_y (μm)	Real Contact Area (μm^2)
0.51	3.23×10^{-6}	-0.811	-1.149	0.811	0.608	23.333	23.243	6.34×10^{-6}

Figure 3. A schematic diagram of misalignment of the contact pad, where the misalignment of the contact pad is measured based on two corners of the mesa: the main corner marked as D_{main} , and the right-up corner marked as D_{up} . The two corners' coordinate are set as (0, 0). In Fig. 3, $D_{\text{main } x} = -0.81 \mu\text{m}$, means the left edge of the contact pad are extend to the left side of the main corner for 0.81 μm .

The measured contact resistance is 0.51 Ω . In COMSOL software, we set up the geometry of CBKR device according to the SEM measurement, and use certain preset-SCR values as input parameters to conduct numerical simulations. With fixed driving current I , through pad 2 to pad 1, (Supplement Fig.1), the simulation could calculate potential difference, ΔV , between pad 3 and pad 2; therefore the expected contact resistance corresponding to the preset-SCR could be extracted as below

$$R_{\text{Expected}} = \frac{\Delta V}{I}$$

Table 2. Preset SCR vs. R_{expected}

preset-SCR ($\Omega \cdot \text{cm}^2$)	9×10^{-3}	1×10^{-2}	2×10^{-2}
R_{Expected} (Ω)	0.059	0.083	1.18

Table 2 shows one set of preset-SCR vs. R_{expected} . Then, compare R_{expected} vs. R_{measured} , the corrected SCR could be narrowed down to a very small range, here between 1×10^{-2} to $2 \times 10^{-2} \Omega \cdot \text{cm}^2$. The final corrected SCR is decided by linear interpolation.

Using CBKR method to measure contact resistance, the sheet resistance should not come into the calculation if there is no misalignment in the device. However, when there is

misalignment in the device, the measured results are different from the real value. But if the sheet resistance is low, the difference between the real value and the measured one is small. In the extreme case, when the sheet resistance is zero (superconductor), the measured value is equal to the real value no matter how big a misalignment is.

When using CBKR method to measure contact resistance, the misalignment is critical because the current path may be altered compared to no misalignment case, and cause an artificial increase or decrease of the measured value. So <50nm misalignment is preferred in industrial environment. However, in academic institutes, the misalignment may be bigger due to the equipment accessibility.

In our case, to estimate how sensitive the corrected SCR value depends on the misalignment, we slightly altered the input misalignment value around the measured ones, and extract the simulation results showing below: Here, in the simulations, only D_x (main) or D_y (main) are increased or decreased by 100 nm around the measured value while the other geometry parameters are kept the same as the measured.

Table 3. The expected contact resistance under slightly altered misalignment.

Condition	preset-SRC ($\Omega \cdot \text{cm}^2$)	5×10^{-3}	1×10^{-2}	1.5×10^{-2}
D_x (main) = -0.711 (μm)	$R_{\text{Expected}} (\Omega)$	0.0733	0.96	
D_x (main) = -0.911 (μm)			0.39	2
D_y (main) = -1.049 (μm)	$R_{\text{Expected}} (\Omega)$	0.076	0.925	
D_y (main) = -1.249 (μm)			0.4	1.98

As the results show, the small error in the measured misalignment gives a corrected SCR in the region of 5×10^{-3} to $1.5 \times 10^{-2} \Omega \cdot \text{cm}^2$. Compared to the original region of 1×10^{-2} to $2 \times 10^{-2} \Omega \cdot \text{cm}^2$, there is no significant change. So small error in the misalignment measurement should not have a big impact in the final corrected SCR value.

Figure 4. Optical microscope images of (a) Hf/Au, (b) Ti/Au and (c) Ni/Au electrodes after annealing at 400 °C.

Figure 5. (a) Cross sectional image using transmission electron microscopy (TEM) image of Ni/Mg₂Si interface as deposited. (b) Cross sectional STEM image of Ni/Mg₂Si interface of the area marked using a red rectangle in (a). (c) EELS line scan along the red arrow show in (b). They all show a clear and sharp interface between the Ni and Mg₂Si films. No inter-diffusion is observed for the as-deposited Mg₂Si/Ni interface.

Table 4. Sample identification for samples used in this study and summary of the bulk resistivities extracted from TLM measurements.

Sample identification	Contact metal	Post annealing condition (°C)	Post annealing time (hours)	Measured specific contact resistivity ($\mu\Omega\text{-cm}^2$)	Bulk resistivity ($\Omega\text{-cm}$)
Ni_none	Ni	N/A	0	5.4 ± 1.9	1.6
Ni_100_N2	Ni	100	2	35.2 ± 11.6	4.8
Ni_200_N2	Ni	200	2	21.5 ± 5.3	50.5
Ni_300_FG	Ni	300	2	5.5 ± 0.5	36.7
Ni_400_FG	Ni	400	2	3.8 ± 0.8	1027.5
Ni_400_FG_24	Ni	400	24	3.0 ± 1.2	776.7
Hf_none	Hf	N/A	0	22.5 ± 8.8	2.3
Hf_300_FG	Hf	300	2	5.8 ± 0.8	40.7
Ti_none	Ti	N/A	0	25.4 ± 7.9	2.1
Ti_300_FG	Ti	300	2	6.9 ± 1.0	13.5
Au_none	Au	N/A	0	241.6 ± 64.7	2.8
Au_100_N2	Au	100	2	251.4 ± 76.3	11.1

Video 1. Slice-and-view 3D topography for Ni/Mg₂Si interface after annealing at 400°C for two hours

Slice-and-view 3D topography.mpg

Start from 12 second, the yellow figure represents the Mg₂Si phase. At 22 second, the blue figure represents both the Ni electrode and the Mg-Si-Ni mixture.

Reference:

- [1] www.comsol.com
- [2] https://en.wikipedia.org/wiki/Continuity_equation#Electromagnetism

Highlights

- Thin film Mg_2Si was prepared using magnetron sputtering.
- Contact resistance was obtained using Cross Bridge Kelvin Resistor method.
- Post deposition annealing effects were also studied.
- Different metal contacts were investigated. Ni shows good stability up to 400°C.
- The degradation mechanism of Ni contact was studied.