

Energimyndighetens titel på projektet – svenska Utveckling av isotropen kiselkarbid och galliumnitrid för energitillämpningar	
Energimyndighetens titel på projektet – engelska Development of isotope-enriched SiC and GaN for energy applications	
Universitet/högskola/företag Linköping University	Avdelning/institution IFM
Adress Linköping 581 83	
Namn på projektledare Olof Kordina	
Namn på ev övriga projektdeltagare Erik Janzén	
Nyckelord: 5-7 st SiC, thermal conductivity, isotope-enriched, MOCVD, power electronics	

Förord

EU Osiris project 2016 – 2020 <https://www.interregeurope.eu/osiris/>

Innehållsförteckning

Sammanfattning	1
Summary	2
Inledning/Bakgrund	2
Genomförande.....	3
Resultat	5
Diskussion	10
Publikationslista	10
Referenser, källor.....	Error! Bookmark not defined.
Bilagor	13

Sammanfattning

Den termiska konduktiviteten i kiselkarbid är ofta refererad dock är det nästan uteslutande konduktiviteten i riktningar vinkelrätt mot kristallens c-axel som refereras. Komponenter som tillverkas i kiselkarbid är dock oftast vertikala i.e. de följer kristallens c-riktning och följdaktligen blir den termiska konduktiviteten i denna riktning av större betydelse.

Den termiska konduktiviteten är kommersiellt mycket viktig eftersom den styr hur stor strömtäthet som kan tillåtas i en komponent. Högre strömtäthet betyder mindre komponenter vilket betyder fler chip per wafer och större vinst för tillverkarna. Men en mindre komponent leder även till lägre kapacitans och således lägre switchförluster.

Termisk konduktivitet är svårt att mäta speciellt på tunna skikt av material med hög termisk ledningsförmåga, och en stor del av projektet ägnades åt att förfinas mätutrustningen och etablera en god metodik för mätning. I projektet mättes den termiska ledningsförmågan upp med god noggrannhet i c-riktningen och vinkelrätt mot c-riktningen i 4H-SiC. Det visar sig att det ofta refererade värdet vinkelrätt mot c-riktningen på 490 W/mK är inkorrekt och det korrekta värdet är 433 W/mK för 4H-SiC. Den termiska konduktiviteten för 3C har också uppmätts på mycket högkvalitativt material. 3C är svårt att mäta just för att materialkvaliteten är så låg. Konduktiviteten för naturlig 3C är 490 W/mK.

Isotopanrikat material förväntas ha högre termisk ledning eftersom man minskar spridning mot atomer med varierande storlek. Isotopeffekten som uttrycks i procent av förhållandet mellan den ökade konduktiviteten och den naturliga konduktiviteten, är 23% vinkelrätt och 16% parallellt med c-riktningen i 4H-SiC samt 8% parallellt med c-riktningen i 6H-SiC. I 3C-SiC var isotopeffekten hela 36% och nådde en på hela 660 W/mK. Endast diamant uppvisar högre termisk ledningsförmåga.

Summary

The value of the thermal conductivity in silicon carbide (SiC) is often referred, however it is almost exclusively the conductivity perpendicular to the crystal's c-axis that is referred. Components that are made of SiC are, however, generally vertical i.e. they follow the crystals c-direction and the thermal conductivity in this direction is consequently of higher importance.

Commercially, the thermal conductivity is of high importance since it controls how high the current density can be allowed in a device. Higher current density means smaller devices which in turn means more chip per wafer and a higher profit for the manufacturers. But a smaller device also leads to a lower capacitance and consequently lower switching losses.

The thermal conductivity is hard to measure especially on thin layers of material with high thermal conductivity, and a large portion of the project was spent on improving the measurement equipment and establishing a good measurement methodology. In the project the thermal conductivity was measured with high accuracy in the c-direction and perpendicular to the c-direction in 4H-SiC. It turns out that the often-referred value of the thermal conductivity perpendicular to the c-direction of 490 W/mK is incorrect and the correct value is 433 W/mK for 4H-SiC. The thermal conductivity for 3C has also been measured on very high-quality material. 3C is difficult to measure especially since the material quality is so low. The conductivity for natural 3C-SiC is 490 W/mK.

Isotope enriched material is expected to manifest a higher thermal conductivity due to reduced scattering against atoms of varying size. The isotope effect which is expressed as a percentage of the ratio between the conductivity increase and the natural conductivity, is 23% and 16% perpendicular and parallel to the c-axis in 4H-SiC, respectively, and 8% parallel to the c-axis in 6H-SiC. In 3C-SiC the isotope effect is a whopping 36% reaching a value of 660 W/mK. This value of the thermal conductivity is only surpassed by diamond.

Inledning/Bakgrund

It is well known that the thermal conductivity (κ) can be enhanced by making the material isotope pure. We have shown that this effect also holds true for SiC measuring a 20% higher κ in isotope pure 4H $^{28}\text{Si}^{12}\text{C}$ compared its natural counterpart. There is some extremely important energy saving applications where this enhanced κ becomes crucial. The AlGaN/GaN HEMT devices for mobile base stations, where a combination of high power and high frequency is required, are perhaps the most striking example where the power efficiency and reliability is largely governed by the κ of the substrate. Mobile data is already estimated to account for 2% of the world's CO₂ emissions¹ and the European Commission estimates that we need to prepare for a factor of 1000 higher data volumes in the very near future. High power devices will also benefit from an increased κ . The current density can be increased making the chip size smaller and/or the performance will be better chiefly on account of the higher electron mobility at the lower junction temperature. In particular, high voltage bipolar devices will benefit from being made on isotope enriched SiC.

When working on isotope enriched materials a common reaction is that the materials will be so expensive that it will never be commercialized. During the current project we have hence identified a way to make the isotope enriched material for these devices **less expensive than the currently used technology produced on natural SiC substrates**. Our research on isotope enriched SiC targets applications where energy may be saved and at the same time finding solutions that will be cost effective.

Genomförande

The project involved the following workpackages:

- SiC epitaxial growth in a hot-wall CVD reactor using a completely new growth concept.
- Investigate isotope enriched 4H-SiC and specifically measure the κ in both directions and compare it to natural 4H-SiC. Investigate if we can detect an increase in the electrical conductivity. This has been done for:
- semi insulating thick layers of importance for high power high frequency applications.
- thick isotope enriched n+ layers of importance for high power applications. Study influence of doping on κ going from n- to n+.

- Investigate the influence of structural defects, like dislocations and stacking faults, on the thermal conductivity.
- Produce SiC n- epi of 4H 30Si13C for possible high-power applications.
- Perform fundamental studies on isotope enriched SiC.
- Explore isotope-enriched GaN.

The hot-wall CVD reactor we used for the growth is world unique equipment and allows to utilize the precursor gases better by reducing parasitic depositions. This is of course of essence when expensive isotope enriched precursors are used.

For the thermal conductivity measurements we employed a Thermal Transient Reflectivity (TTR) technique (Figure 1). The technique uses a probe laser and a pulse laser where the beam diameter of the probe laser is significantly smaller than that of the pulsed laser which generates the heat. The sample is deposited with a layer of gold that will absorb the heat from the pulsed laser and reflect the probe laser beam. Since Au has a linear coefficient of thermal reflection at the wavelength of the probe laser (488 nm), the temperature of the Au after a pulse can be measured by the difference in reflectance from the steady state. Collecting the response after several pulses and averaging these gives a transient which can be fitted using two unknown parameters which are the thermal resistance of the metal semiconductor interface and κ of the semiconductor under study. The technique only measures the top few micrometers which makes it possible to study thin layers. In fact this technique can also be used to measure the thermal boundary resistance created by the AlN nucleation layer.

The growth and thermal conductivity measurements were performed by the PI, Dr. Olle Kordina and PhD student Björn Lundberg. Prof. Erik Janzén was in charge of the defect and doping investigations. Dr. Ivan Ivanov was responsible for the optical (PL, PLE, etc) investigations. Theoretical predictions of thermal conductivity using first principle calculations were performed by Prof. Igor Abrikosov and Dr. Olle Hellman.

On the isotope pure precursors and growth of isotope enriched precursors we have collaborated with the following international partners:

- Professor Joel Ager, Lawrence Berkley National Labs
- Dr. Dag-Øistein Eriksen, Isosilicon A/S
- Dr. Gro Eide, Elkem A/S

The thermal conductivity measurements and analysis activities were supported by international collaborations:

- Professor Peter Raad, Southern Methodist University, Dallas, TX, USA
- Professor Martin Kuball, Bristol University, UK

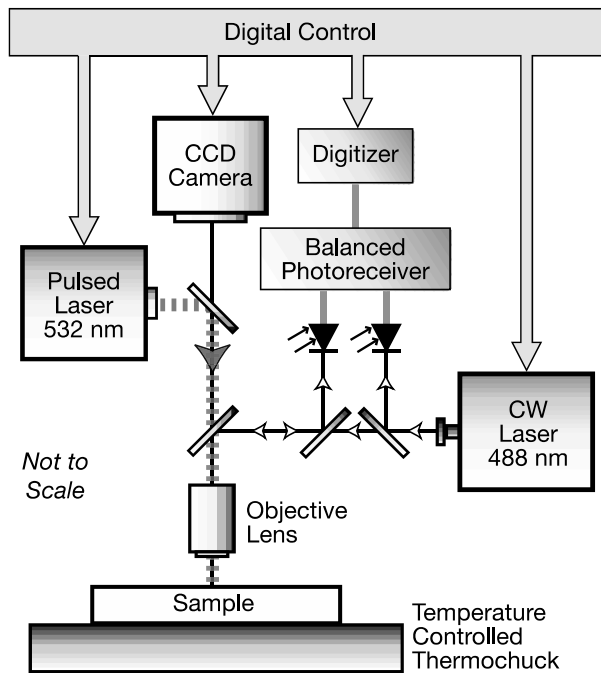


Figure 1 Functional Schematic of the Transometer™ Pump-and-Probe System.

Resultat

Thermal conductivity of isotope enriched SiC as a function of polytype

We grew the SiC samples using isotopically enriched carbon and silicon precursor gases in a chloride based hot-wall chemical vapor deposition process known to produce high quality samples. Films were grown on substrates of the most common polytypes and orientations. Large single-crystal 3C samples were used as substrates for the cubic samples, enabling us to produce films of excellent structural quality. One 4H layer was grown using only isotope enriched silicon precursor and a carbon source with natural isotope abundance. Using photoluminescence, we measured the doping levels which were found to be in the order of 10^{15} cm^{-3} and primarily consisting of nitrogen, which is to be expected for SiC grown this way. Secondary ion mass spectroscopy measurements showed that the degree of isotopic enrichment in the grown material was 99.98% and 99.85% for ^{12}C and ^{28}Si respectively.

Polytype	Cut	Isotope distribution	Thickness (μm)	Doping level (cm^{-3})	κ (W/mK)	% increase	Reference
4H	a-cut	Natural	28	$3 \cdot 10^{15}$	433	-	This work
4H-4°	c-cut	Natural	30	$1 \cdot 10^{15}$	361	-	This work
4H	a-cut	Enriched	30	$3 \cdot 10^{15}$	535	23	This work
4H-4°	c-cut	Enriched	28	$1 \cdot 10^{15}$	420	16	This work
4H-4°	c-cut	Enriched Si	200	$1 \cdot 10^{15}$	405	12	This work

4H		Natural	Bulk			-	Carter Jr <i>et al.</i> ²²
	a-cut			$5 \cdot 10^{15}$	480		
4H		Natural	Bulk	Semi		-	Carter Jr <i>et al.</i> ²²
	c-cut			Insulating	330		
4H		Natural	Bulk			-	Carter Jr <i>et al.</i> ²²
	c-cut			$2 \cdot 10^{18}$	330		
4H	c-cut	Natural	2000	$5 \cdot 10^{18}$	349	-	Wei <i>et al.</i> ³⁰
4H	c-cut	Natural	2000	$5 \cdot 10^{17}$	270	-	Wei <i>et al.</i> ³⁰
6H	a-cut	Natural	3000	-	440	-	This work
6H-3.5°	c-cut	Natural	28	$3 \cdot 10^{15}$	357	-	This work
6H-3.5°	c-cut	Enriched	28	$3 \cdot 10^{15}$	386	8	This work
6H	a-cut	Natural	3500	$1 \cdot 10^{17}$	490	8	Slack ¹⁹
6H	a-cut	Natural				-	Burgemeister <i>et al.</i> ³¹
			1000	$5 \cdot 10^{16}$	387		
6H	a-cut	Natural				-	Burgemeister <i>et al.</i> ³¹
			1000	$1 \cdot 10^{19}$	295		
6H	a-cut	Natural				-	Burgemeister <i>et al.</i> ³¹
			1000	$5 \cdot 10^{18}$	250		
6H	a-cut	Natural				-	Burgemeister <i>et al.</i> ³¹
			1000	$5 \cdot 10^{19}$	231		
6H	a-cut	Natural				-	Burgemeister <i>et al.</i> ³¹
			1000	$1 \cdot 10^{20}$	142		
6H	a-cut	Natural				-	Carter Jr <i>et al.</i> ²²
			Bulk	$3.5 \cdot 10^{17}$	380		
6H	a-cut	Natural	Bulk			-	Carter Jr <i>et al.</i> ²²
				$1.4 \cdot 10^{16}$	400		
6H	c-cut	Natural	Bulk			-	Carter Jr <i>et al.</i> ²²
				$1.5 \cdot 10^{18}$	300		
6H	c-cut	Natural	Bulk			-	Carter Jr <i>et al.</i> ²²
				$3.5 \cdot 10^{17}$	320		
6H	a-cut	Natural	Bulk			-	Morelli <i>et al.</i> ²⁹
				$3.5 \cdot 10^{16}$	430		
6H	a-cut	Natural	Bulk			-	Morelli <i>et al.</i> ²⁹
				$2.9 \cdot 10^{18}$	300		
6H	c-cut	Natural	2170			-	Nilsson <i>et al.</i> ³²
				$5 \cdot 10^{17}$	330		
3C	[111]	Natural	28	-	490	-	This work
3C	[111]	Enriched	28	-	656,669	36	This work
3C	Polycrystal	Natural	-	-	330	-	Morelli <i>et al.</i> ²⁴

Material	Isotope enrichment	Thermal Improvement @RT	Conductivity	Reference
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Silicon, ^{28}Si	99.983%	10%	Inyushkin <i>et al.</i> ³³
Silicon, ^{28}Si	99.982%	10%	Kremer <i>et al.</i> ³⁴
Silicon, ^{28}Si	99.7%	60%	Capinski <i>et al.</i> ³⁵
Diamond, ^{12}C	99.9%	50%	Anthony <i>et al.</i> ³⁶
Germanium, ^{70}Ge	99.99%	20%	Ozhogin <i>et al.</i> ³
Germanium, ^{70}Ge	99.99%	30%	Asen-Palmer <i>et al.</i> ³⁷

In the tables, we show measurements on natural and enriched samples grown at LiU and from other work.

Based on our research results we conclude the following:

The thermal conductivity for natural 4H-SiC in the basal plane (a-cut) is reported to be 480 and 490 W/mK by Crter *et al.* and Slack, respectively. We argue that these values do not represent the correct thermal conductivity (they could not be reproduced by any other researcher). Instead, we conclude that the thermal conductivity values (have been verified in many ways) are 433 and 440 W/mK for 4H- and 6H-SiC, respectively.

The thermal conductivity value in the c-direction varies a bit between different groups and measurement techniques. For natural 4H-SiC we see values of 330 W/mK from Carter *et al.* and 349 and 270 W/mK from Wei *et al.* Our value for natural 4H-SiC in the c-direction is 361 W/mK which is close to the values given by Carter *et al.* Carter *et al.* made their measurements using laser flash which is not so suitable to use for wafers in the c-direction.

Natural 6H-SiC in the c-direction varies between 300 and 320 W/mK in the literature, but just like the case of 4H-SiC in the c-direction, there are very few reports. Our value for 6H-SiC in the c-direction is 357 W/mK which is higher than what has been reported by others.

The isotope effect for 4H-SiC is 23% and 16% for the basal plane and c-direction, respectively. As can be seen, the isotope effect is weaker in the c-direction where the structure is more complex.

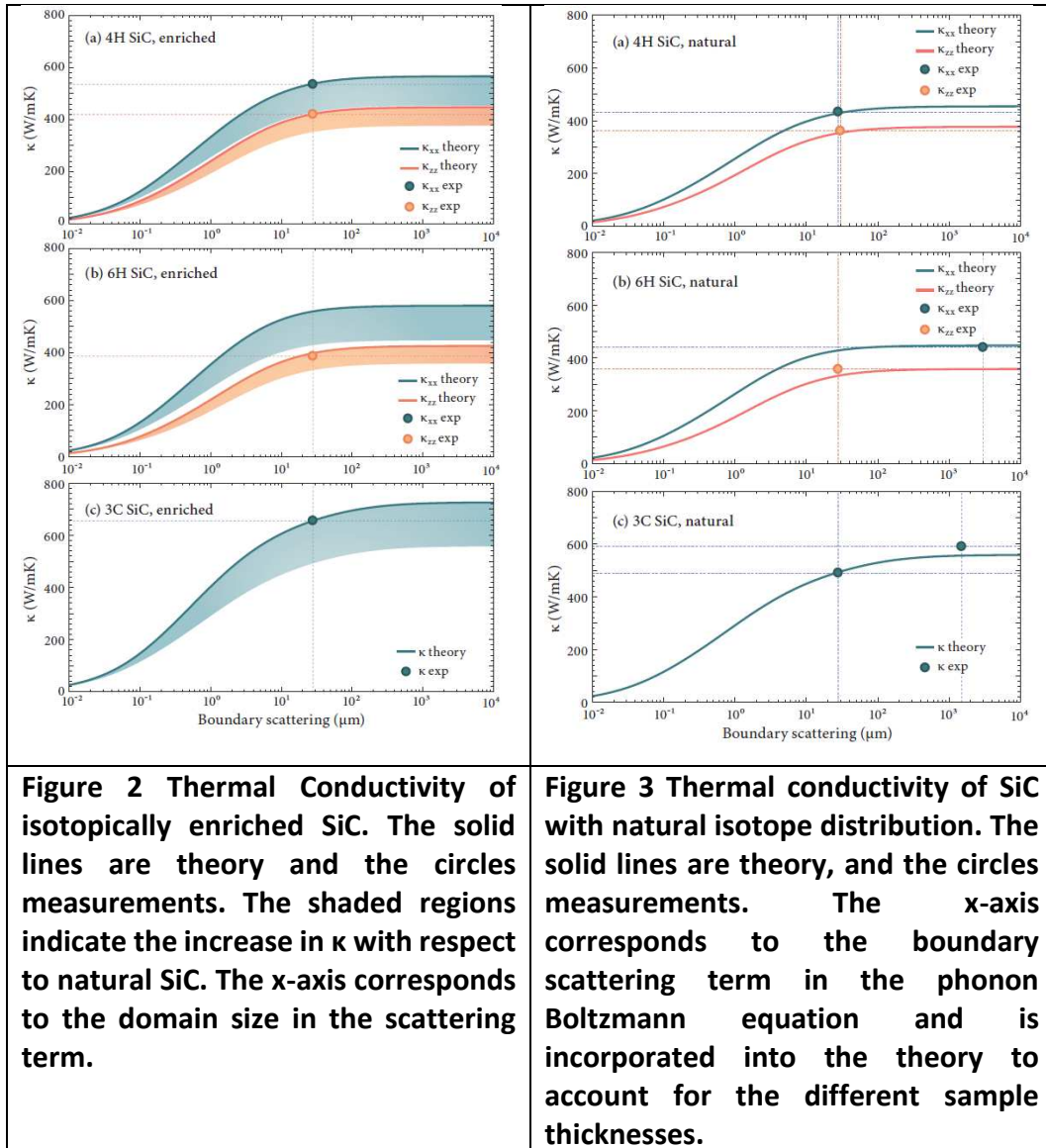
In 6H-SiC, the isotope effect is only 8% in the c-direction. No sample was grown on the basal plane since no substrate could be obtained. The isotope effect in the basal plane for 6.

Our experimental measurements clearly show that isotope enrichment increases the thermal conductivity of silicon carbide and the results match calculated values very well. The magnitude of the improvement varies with polytype and crystal direction. In general terms, it is larger in high symmetry directions with smaller unit cell size where the probability of phonons scattering is already lower. This is clearly seen for the cubic polytype, which our measurements reveal has the highest thermal conductivity of the polytypes and which benefitted the most from enrichment with a 36% increase and a maximum value of 669 W/mK, beaten only by diamond.

In addition, we have demonstrated that using an enriched silicon precursor with a natural carbon source still has a beneficial effect. This is important, as carbon contamination from eg. reactor parts may be difficult to avoid completely in any attempt at production on a larger scale.

Thermal conductivity of isotope enriched SiC as a function of polytype

Even more excitingly, we have demonstrated both theoretically and experimentally that the thermal conductivity of isotope-enriched 3C-SiC (111) increases by 34% - 36% compared to its natural counterpart.



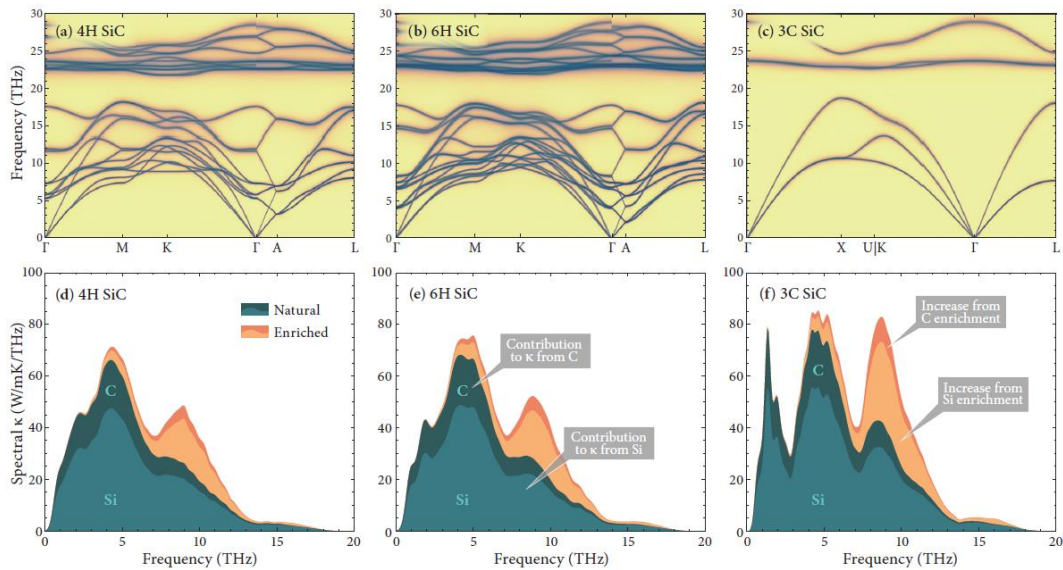


Figure 4 Atom and frequency resolved thermal conductivity at room temperature. The blue regions correspond to natural SiC and the orange regions to enriched SiC. The increase in thermal conductivity due to isotope enrichment is centered around 9THz, corresponding to a range in frequencies where anharmonic damping is large. The 4H and 6H polytypes behave similarly, but the cubic 3C shows a markedly larger response in the region around 9THz.

Diskussion

Isotope enriched materials are known to improve the thermal conductivity and this work has shown that significant improvements can be obtained on isotope enriched SiC. A high thermal conductivity will improve the performance of a device in several ways:

- The high thermal conductivity will reduce the temperature at the junction which improves the mobility and hence reduces the resistance at the operating temperature.
- The improved thermal conductivity can also allow a higher current density which reduces the size of the device which reduces the capacitance and hence reduces the switching losses.

Of course, increasing the current density will counteract the reduction of temperature at the junction. Hence, a new device design needs to be made where the losses are minimized based on the new thermal behavior of the material.

Some of the material that was generated in this project together with a horizon 2020 project called Osiris was used to establish the improvement of a GaN-on-SiC high electron mobility transistor (HEMT) device. The SiC had to be semi-insulating (SI) and considerable effort was spent in perfecting the on-axis SI SiC layer. This was polished and then a GaN HEMT structure was grown and processed into transistors. It showed that a significant temperature reduction of around 10% could be measured on the isotope enriched material. However, the

result did not show the full potential of the isotope enriched material which was believed to be due to structural defects introduced when the SI SiC was grown.

Yet, a reduction of temperature by such an amount is equivalent to around 20 °C lower operating temperature which improves the lifetime of the device by one order of magnitude and the on-state losses are reduced by about 10%. More efficient high frequency devices are crucial for a more sustainable society where wireless communication is increasing exponentially. According to a study, the internet which includes data centers, wireless communication, terminals, and the production of ICT, is predicted to consume 20% of the total electricity demand in 2030. GaN-on-SiC is one technology that is expected to improve the efficiency particularly in combination with massive MIMO technology where the GaN-on-SiC HEMT is considered an enabler, enormous amounts of energy may be saved.

However, the efficiency and power density of the HEMT is largely governed by the thermal conductivity of the substrate and substantial efforts are being made to put GaN on diamond which can improve the power density further. The isotope enriched SiC can be a serious alternative to GaN on diamond for high performance applications.

In order to make an impact on the environment, mass production of the material must be made, and, in this case, a low-cost enrichment method must be developed. A company in Norway which is in collaboration with LiU has developed a method using zeolites to enrich silane directly. This method could produce isotope enriched material in adequate volumes and at low cost.

The next issue is making the SI SiC which was done using chemical vapor deposition (CVD) in this project. The efficiency was only 5% i.e. 95% of the expensive precursors were simply passed through the reactor. A horrible waste. Other methods could be used to greatly improve the efficiency. For instance, the isotope enriched gases can be introduced into a fluidized bed to produce polycrystalline isotope enriched SiC. The powder can subsequently be used in close space sublimation. The efficiency of the whole process can be higher than 50% which would make the cost to produce the material low enough for volume production.

Publikationslista

Patents:

Isotope enriched silicon carbide with enhanced thermal conductivity for energy applications. PCT/SE2014/050807. This patent describes a way to produce isotope enriched SiC. The isotope enriched substrates have a higher thermal conductivity and would hence help dissipate heat and make devices more efficient.

Inexpensive semi insulating substrates, Swedish application 1430022-2. PCT/SE2014/050807. This patent describes how to produce less expensive semi-insulating substrates. These substrates are very expensive to purchase today and

is our greatest cost. The patent also describes making these substrates isotope enriched. The patent authority felt that this was two inventions and recommended that this patent is split into two. I am checking the latest information about this.

Manuscripts to be submitted for publication

Superior SiC Thermal Conductivity through Isotope Enrichment

By Olle Hellman, Björn Lundqvist, Jawad Ul-Hassan, Valdas Jokubavicius, Ivan Ivanov, Igor Abrikosov and Olof Kordina

Through-Plane Thermal Conductivity of 4H Silicon Carbide

By Björn Lundqvist, Peter E. Raad, Pavel L. Komarov, Ivan G. Ivanov, Olof Kordina

Journal articles

[Growth Mechanism of SiC Chemical Vapor Deposition: Adsorption and Surface Reactions of Active Si Species](#)

By: [Sukkaew, Pitsiri](#); [Kalered, Emil](#); [Janzen, Erik](#); et al.

[JOURNAL OF PHYSICAL CHEMISTRY C](#) Volume: 122 Issue: 1 Pages: 648-661 Published: JAN 11 2018

[Silicon Chemistry in Fluorinated Chemical Vapor Deposition of Silicon Carbide](#)

By: [Stenberg, Pontus](#); [Sukkaew, Pitsiri](#); [Farkas, Ildiko](#); et al.

[JOURNAL OF PHYSICAL CHEMISTRY C](#) Volume: 121 Issue: 5 Pages: 2711-2720 Published: FEB 9 2017

[Ab Initio Study of Growth Mechanism of 4H-SiC: Adsorption and Surface Reaction of C₂H₂, C₂H₄, CH₄, and CH₃](#)

By: [Sukkaew, Pitsiri](#); [Danielsson, Orjan](#); [Kordina, Olof](#); et al.

[JOURNAL OF PHYSICAL CHEMISTRY C](#) Volume: 121 Issue: 2 Pages: 1249-1256 Published: JAN 19 2017

[Vector Magnetometry Using Silicon Vacancies in 4H-SiC Under Ambient Conditions](#)

By: [Niethammer, Matthias](#); [Widmann, Matthias](#); [Lee, Sang-Yun](#); et al.

[PHYSICAL REVIEW APPLIED](#) Volume: 6 Issue: 3 Article Number: UNSP 034001 Published: SEP 8 2016

[Vector Magnetometry Using Silicon Vacancies in 4H-SiC Under Ambient Conditions](#)

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[PHYSICAL REVIEW APPLIED](#) Volume: 6 Issue: 3 Article Number: UNSP 034001 Published: SEP 8 2016

[Optical properties and Zeeman spectroscopy of niobium in silicon carbide](#)

By: [Gallstrom, Andreas](#); [Magnusson, Bjorn](#); [Leone, Stefano](#); et al.

[PHYSICAL REVIEW B](#) Volume: 92 Issue: 7 Article Number: 075207 Published: AUG 27 2015

[Brominated Chemistry for Chemical Vapor Deposition of Electronic Grade SiC](#)

By: [Yazdanfar, Milan](#); [Danielsson, Orjan](#); [Kalered, Emil](#); et al.

[CHEMISTRY OF MATERIALS](#) Volume: 27 Issue: 3 Pages: 793-801 Published: FEB 10 2015

[Carrier Lifetime Controlling Defects Z\(1/2\) and RB1 in Standard and Chlorinated Chemistry Grown 4H-SiC](#)

By: [Booker, Ian D.](#); [Ul Hassan, Jawad](#); [Lilja, Louise](#); et al.

[CRYSTAL GROWTH & DESIGN](#) Volume: 14 Issue: 8 Pages: 4104-4110 Published: AUG 2014

[On the use of methane as a carbon precursor in Chemical Vapor Deposition of silicon carbide](#)

By: [Yazdanfar, M.](#); [Pedersen, H.](#); [Sukkaew, P.](#); et al.

[JOURNAL OF CRYSTAL GROWTH](#) Volume: 390 Pages: 24-29 Published: MAR 15 2014

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