

Synthesis of Ni–Ga Alloy Nanoparticles *in situ* for CO₂ Hydrogenation

Author: Fjalar Högnason Loodberg
fj3825ho-s@student.lu.se

Supervisors: Tianyi Hu
tianyih.hu@chem.lu.se

Kimberly Dick Thelander
kimberly.dick_thelander@chem.lu.se

Examiner: Martin Ek Rosén
martin.ek@chem.lu.se

Spring 2024



LTH
FACULTY OF
ENGINEERING

Abstract

Nickel gallium alloys have recently been discovered as a promising material for the catalyzation of methanol synthesis from carbon dioxide. Due to the novel nature of the material system for this purpose, there is a large potential for optimization in terms of catalytic activity and selectivity for methanol. Optimization through engineering of phases and facets in such materials is often difficult due to the limited information *ex situ* synthesis can yield about the mechanisms of formation. This study aims to elucidate the synthesis dynamics of nickel gallium alloys to support the development of more optimized catalysts in the future. This is done through the use of environmental transmission electron microscopy, a transmission electron microscope combined with a metal-organic chemical vapor deposition system to enable atomic resolution imaging of synthesis *in situ*. 30 nm diameter nickel nanoparticles were supplied gallium *via* the metal-organic trimethylgallium in gas phase at different flow rates and at varied elevated temperatures. A flow varied between 33 and 50 nmol_{TMGa}/min with a substrate temperature of 300 to 400 °C yielded Ni₂Ga₃ phase particles with clear facets and pure gallium droplets on the substrate after 40 min. This indicates that these parameters are too high for synthesis of the reportedly optimal Ni₅Ga₃ phase. At a flow of 6 nmol_{TMGa}/min, 400 °C, a nanoparticle with composition ~75:25 nickel to gallium ratio was observed changing to ~65:35 through growth of a new faceted region over the course of 12 min. Here, the phases both before and after the observed event could not be determined. A flow of 23 nmol_{TMGa}/min, 600 °C, yielded what is presumed to be Ni₅Ga₃ after a 6 min transformation from pure nickel. This indicates that the potentially desirable Ni₅Ga₃ phase is possible to synthesize in this environment, and could warrant further study. The rate of gallium incorporation into the particles was also indicated to depend on temperature and gas flow. More studies are needed in order to pinpoint specific conditions for synthesis of different phases, and to decouple the temperature and gas flow parameters. Synthesized particles were also analyzed in the presence of CO₂ in an attempt to observe the actual catalytic process *in situ*, however oxygen impurities in the gas and a lack of control over the flow limited the usefulness of this experiment.

When & where

The project was conducted as part of a Master's Degree in Engineering, Engineering Nanoscience during the spring (January-June) of 2024 in the Inorganic Nanomaterials Group of the Centre for Analysis and Synthesis at Lund University, Faculty of Engineering. This was under the supervision of PhD student Tianyi Hu and professor Kimberly Dick Thelander, and with associate senior lecturer Martin Ek Rosén as examiner. ETEM experiments were conducted on the following dates:

2024-02-12, 2024-02-16, 2024-03-07, 2024-03-21, 2024-04-19

The oral presentation of the project is planned to take place on 2024-06-10 at 10:00 in the coffee room at the Centre for Analysis and Synthesis.

Acknowledgements

These are all the people I want to thank, either for being helpful in the making of this thesis, or for being helpful in my life. I want to give my thanks to...

...Tianyi for being with me every step of the way during our experiments, and always being open to answering questions and helping with analysis.

...Kimberly for giving me the opportunity to work in this research group, and for fostering such a nice atmosphere in the group.

...Mehran for kindly providing the nickel nanoparticles that were used for most of the experiments.

...Miķelis for giving invaluable advice on writing and analysis as well as the incessant asking of if I was done with my thesis.

...Azemina, Aidas & Hedda for being great office mates. I think it is safe to say that we are experts in daily online guessing games at this point.

...Martin for being my introduction to university level chemistry, and for giving such a daunting field a friendly and welcoming face.

...my friends from *n19*, without whom I never would have gotten myself through five years of studies. Spending time together with you both in and outside university has made this the best time of my life so far.

...my siblings and my dad for never doubting me, even when I have. And lastly to my mom, who I wish could've seen me reach this milestone in my life. Miss you.

Abbreviations & terms

in situ "on site" in latin, here meaning the observation of a process while it is happening

ex situ the opposite of *in situ*; observation after a process has already taken place

CCUS Carbon Capture Utilisation and Storage

CO₂ Carbon Dioxide

EDS Energy Dispersive X-ray Spectroscopy

ETEM Environmental Transmission Electron Microscopy

FFT Fast Fourier Transform

Ga Gallium

GaO_x Gallium Oxide

H₂ Hydrogen Gas

HRTEM High Resolution Transmission Electron Microscopy

MEMS Microelectromechanical System

MOCVD Metal-Organic Chemical Vapor Deposition

Ni Nickel

Ni–Ga Nickel Gallium

SCCM Standard Cubic Centimeter per Minute

SiN_x Silicon Nitride

TEM Transmission Electron Microscopy

TMGa Trimethylgallium

Figures

1	Schematics explaining the principles behind EDS analysis.	4
2	The Ni–Ga binary phase diagram. Used with permission from Springer Nature and retrieved from Okamoto et. al.[18].	7
3	Schematics of the ETEM and MEMS chips.	8
4	Diagram of the gas handling system. Gas supplies not used in this study are grayed out. Note that the CO ₂ source is separate from the rest of the system and is controlled solely by a manual valve. Used and modified with permission by Sjökvist [22].	10
5	Two nanoparticles synthesized using a high flow of TMGa and their respective FFTs with simulated diffraction patterns overlayed.	11
6	HRTEM images of phase transformation in Ni–Ga nanoparticle under 6 nmol _{TMGa} /min at 400 °C in 2 min intervals. Focus was readjusted for images in 6f and 6g. Blue circles in 6a indicate regions where EDS spectra have been collected.	12
7	FFTs and highlighted regions of Ni–Ga nanoparticle before and after the transformation displayed in figure 6. Red and green circles in FFTs show the spots used for the respective colored highlights in the realspace images.	13
8	HRTEM images of phase transformation of Ni nanoparticle to Ni–Ga alloy under 23 nmol _{TMGa} /min at 600 °C in 1 min intervals from the moment gas supply was started (figure 8a), up until the 6 minute mark when transformation had stopped (figure 8g).	14
9	FFTs and matching simulated diffraction patterns of Ni nanoparticle before and after exposure to 23 nmol _{TMGa} /min at 600 °C for 6 min.	15
10	Composition of random sample of particles according to EDS after 23 nmol _{TMGa} /min was supplied for 10 min at 600 °C without the electron beam.	15
A1	NiAs nanoparticles observed forming from Ni nanoparticles and AsH ₃ contaminants.	A
A2	Comparison between two sizes of aperture. The red circles indicate the ROI where electron dose has been calculated. The beam is more condensed in the image with the smaller aperture.	B
A3	Diagram of the general method for matching an HRTEM image with a specific compound.	C

Contents

Abstract	i
When & where	ii
Acknowledgements	ii
Abbreviations & Terms	iii
Figures	iv
Contents	v
1 Background	1
2 Goal	1
3 Theory	1
3.1 Transmission electron microscopy	1
3.1.1 High resolution transmission electron microscopy	2
3.1.2 Diffraction imaging	3
3.1.3 Energy dispersive X-ray spectroscopy	3
3.1.4 Beam effects	4
3.2 Environmental transmission electron microscopy	4
3.2.1 Metal-organic chemical vapor deposition	4
3.2.2 Microelectromechanical systems in TEM	5
3.3 Nickel gallium binary system	5
4 Method	7
4.1 Equipment used	7
4.2 Sample preparation	8
4.3 General experimental procedure	9
4.4 Gas handling system	9
4.5 Data processing	10
5 Results	11
5.1 High TMGa flow	11
5.2 Low TMGa flow	12
5.3 Observation with CO ₂	16
6 Discussion	16
6.1 Phase and facet engineering	16
6.2 Beam effects	17
6.3 Contamination	17
6.4 Possible shortcomings and improvements	18
7 Conclusions and outlook	19
8 References	20
Appendix A: Nickel arsenide particles	A
Appendix B: Dose comparison between aperture sizes	B
Appendix C: Matching crystal structures	C

1 Background

Climate change stands to be some of the largest challenges humanity will face in the 21st century. It has already caused significant loss of life and irreversible damage to nature, and changes responsible for this will continue to intensify if mitigating efforts are not made. As the authors of the 2023 International Council for Climate Change (IPCC) report write; "Deep, rapid, and sustained mitigation and accelerated implementation of adaptation actions in this decade would reduce projected losses and damages for humans and ecosystems" [1].

The main way of tackling this crisis will be to reduce the emissions of greenhouse gases, although a reduction in emissions might not be enough. The International Energy Agency (IEA) reports that carbon capture and storage (CCUS) technology is essential for reaching the goal of net zero emissions [2]. As of 2022, CO₂ is the most commonly emitted greenhouse gas amounting to roughly 75% of the global warming potential of all anthropogenic greenhouse gas emissions [3], and technology already exists today for capturing emitted CO₂ and either putting it into long-term storage (the S in CCUS), or using it for another purpose (the U in CCUS). The reason the IEA gives for CCUS being essential is some industries being very difficult to decarbonize, such as cement and steel production. Deployments are trailing behind what would be needed to limit global warming to 2 °C, and implementation faces both technological and economic challenges. Progress in the field of CCUS could help to overcome these challenges.

One method for utilizing emitted CO₂ that exists today is hydrogenation into higher value carbon products through catalysis. The material Cu/ZnO/Al₂O₃ is an optimized catalyst for converting CO₂ and H₂ into methanol, which is heavily used as a chemical feedstock in industry, can function as a fuel, or as storage of energy [4]. The synthesis process does however require high pressures and temperatures which makes it costly and limits it to large scale centralized facilities [5]. Nickel-gallium-based (Ni–Ga) alloys have recently been discovered as potential improved replacement for the currently used catalysts for conversion of CO₂ into methanol [6]. Initial testing of these new catalysts promise function at ambient pressure and much lower temperatures which could enable small scale production of methanol at sites where CO₂ is emitted using locally produced green hydrogen. Selectivity for methanol over the byproduct CO is also shown to be higher, which would lead to higher yields.

2 Goal

The goal of this study is to synthesize Ni–Ga nanoparticles *in situ* using environmental transmission electron microscopy (ETEM) and metal-organic chemical vapor deposition (MOCVD), with a focus on the formation of phases under different gas supply conditions and temperatures. An understanding of the formation dynamics of these catalysts could give insights into how to optimize their catalytic function in the future. A secondary goal is to observe synthesized particles while active in synthesis by supplying CO₂. This will hopefully shed some light on the formation mechanisms and viability of MOCVD as a synthesis method for Ni–Ga alloys, for continued research or perhaps industrial use. Observing the morphology and phases present in synthesized particles has a possibility to inform future optimization efforts of these materials as the most active facets and phases have currently not been definitively determined.

3 Theory

This section describes some theory behind transmission electron microscopy (TEM), environmental transmission electron microscopy (ETEM), and the Ni–Ga binary system. Parts regarding TEM are based mostly on information found in *Transmission Electron Microscopy* by Williams & Carter [7].

3.1 Transmission electron microscopy

A fundamental limiting factor for the resolution of visible light microscopy is the wavelength of light used. The maximum resolution can, using the Rayleigh criterion, be approximated to roughly half of

the wavelength of light used. Since the shortest visible wavelength to the human eye is around 400 nm, resolution is typically limited to ~ 200 nm. While certainly enough for many applications, it bars the use of optical microscopy from analysis of nanoscale structures, which are typically defined as ranging from 1 to 100 nm in size in at least one dimension.

Transmission electron microscopy is an analysis technique used to image small amounts of material at the nanoscale. The use of electrons as opposed to photons like in traditional optical microscopy allows for much higher resolution, as well as providing the option of using additional analysis techniques utilizing additional signals generated from the electron beam interacting with the sample. Electrons in TEM have a wavelength in the order of picometers (10^{-12} m), although the resolution is typically in the order of ångström (10^{-10} m) due to other limiting factors than the wavelength.

Electron microscopes use electromagnets as analogs to optical lenses. Instead of relying on a change in refractive index, these influence the path that the electrons take via the Lorentz force, the force a charged particle in movement experiences when passing through a magnetic field. By varying the current in the electromagnets, the strength of the field can be changed, and thus also the "power" or focal length of the electromagnetic lenses. Aligning an electron microscope essentially involved tuning the lenses in the top half of the microscope to form a parallel beam to illuminate your sample, and adjusting the lenses below your sample to project the beam now holding the image of your sample onto a fluorescent screen or camera sensor.

The most important parts of a standard TEM listed from top to bottom are:

- an electron gun which produces electrons at a set current and also accelerates them to the desired energy (typically 100-300 keV)
- a set of condenser lenses and a condenser aperture which together control the size and brightness of the beam
- the sample itself
- an objective lens which forms the image (and diffraction pattern) of the sample and controls the focus
- intermediate and projector lenses to magnify the image of the sample
- and finally a fluorescent screen or a camera sensor to pick up the image

All of these components must be under high vacuum as to not disturb the path of the electrons. This setup alone makes a typical TEM a quite bulky piece of equipment, on the order of several meters tall and a column diameter of ~ 30 to 50 cm.

3.1.1 High resolution transmission electron microscopy

High resolution transmission electron microscopy is the term used to describe bright-field imaging at high magnification and resolution. The electron beam reaches the sample in a parallel and in phase. Individual atoms contribute to a phase difference when the electrons eventually reach the screen or camera, resulting in constructive and destructive interference and the atomic lattice becoming visible. One thing to keep in mind is that the interference can cause atoms to be represented by *either* dark spots *or* light spots, depending on the focus and the shape of the contrast transfer function. Either way, these spots can be used to determine the distance between atoms and planes of atoms which is a powerful tool in analysis.

3.1.2 Diffraction imaging

One common analysis method for crystalline materials in TEM is the use of diffraction patterns to determine the structure of a sample. Diffraction patterns can be imaged in the back-focal plane of the objective lens. In the case of a sample consisting of a single thin crystal with a high symmetry direction aligned with the optical axis, this will be an array of spots which correspond to the symmetries and plane spacings of the atoms within. The distance of a spot from the center of the image corresponds to the reciprocal of the plane spacing in a specific crystallographic direction.

Diffraction space (also known as reciprocal space, frequency space...), meaning the space in which a diffraction pattern is visible, is analogous to the Fourier transform of the realspace image. By taking the 2D discrete Fourier transform (often simply called the FFT due to the type of algorithm used, a Fast Fourier Transform) of a realspace TEM image, one can get an image similar to the diffraction space image of the same area. While subject to a different class of aberrations due to being digital, it can be a much simpler and quicker way of collecting the same information.

As a note on terminology, any time the abbreviation "FFT" is used in this thesis, it could perhaps be more accurately be substituted with "2D discrete Fourier transform" as FFT is technically the name for the type of computer algorithm used to calculate the transform. The choice to still use "FFT" rather than "DFT" or "2D-DFT" is done due to familiarity and to avoid any confusion with Density Functional Theory, which is briefly mentioned in section 3.3. The term "realspace" is sometimes used to distinguish regular images from their FFT counterparts.

3.1.3 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS) is a technique for acquiring qualitative and quantitative chemical information about a sample in electron microscopy. A sensor is used to measure so-called characteristic X-rays emitted by a sample under electron beam illumination.

A high energy electron from the microscope beam transfers its energy to a core electron in an atom of the sample. This causes the core electron to be ejected from the sample and leave an empty state. This empty state is then filled by a higher energy electron. The excess energy from the decrease in potential is released as a photon of energy specific to that transition. A schematic of the process in the inner shells of an atom is shown in figure 1a. An element typically has a handful of probable transitions, creating a spectrum of photon energies indicative of that specific element. By comparing the amplitudes of peaks belonging to specific elements, the relative composition of a sample can also be determined. A spectrum of a sample containing a few elements is shown in figure 1b.

It is of high importance to consider the accuracy of EDS measurements, which can be influenced by a number of factors. The most important is perhaps the number of X-rays collected in the relevant peaks, where a low count can lead to the signal not being distinguishable from noise. For that reason, lighter elements such as nitrogen and oxygen that do not give a very strong X-ray signal are harder to detect both qualitatively and especially quantitatively. Channeling has been shown to have an effect on the reported relative composition in III/V nanowires aligned to zone axis [8], one could speculate the same effect could happen in an aligned nanoparticle of a binary alloy. The spatial resolution of EDS measurement in TEM is also limited by the size of the electron beam and its excitation volume. It can therefore be important to condense the electron beam so that only the region of interest is illuminated when doing EDS.

The strobe peak, meaning the tall peak close to 0 eV in energy of an EDS spectrum (figure 1b), is part of the background noise of an EDS spectrum. It is made up partly of electronic noise, and partly of photons resulting from black-body radiation. The wavelength of black-body radiation is related to the temperature of the emitting material, which can be used for temperature calibration and is mentioned briefly in section 3.2.2.

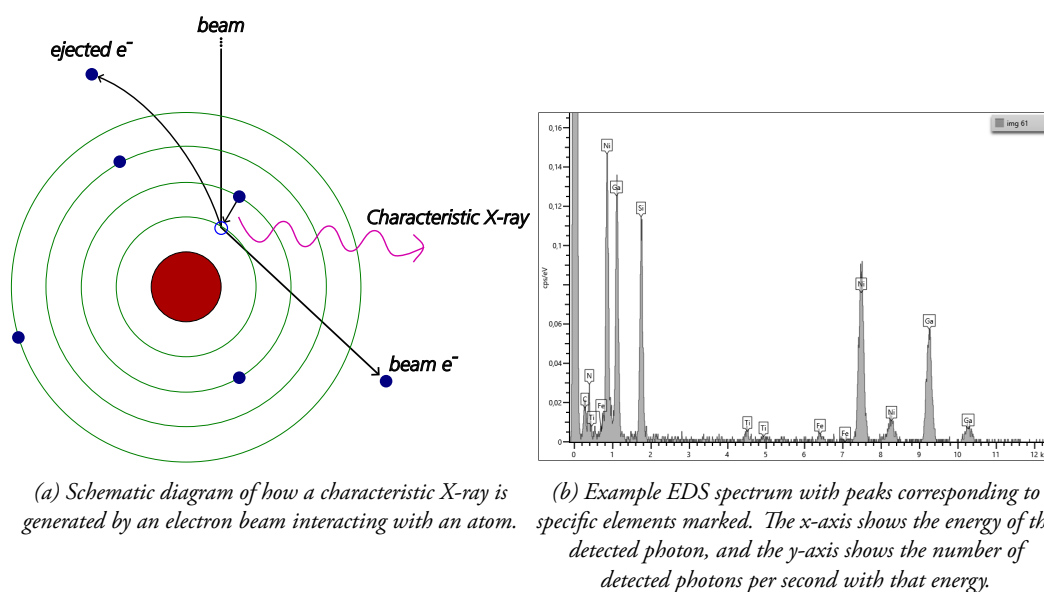


Figure 1: Schematics explaining the principles behind EDS analysis.

3.1.4 Beam effects

Beam damage is an umbrella term for different processes through which the electron beam permanently changes the specimen it is used to analyze. The word "damage" stems from these changes in the sample historically been seen as detrimental to the analysis as the material is not necessarily the same as what it started as. This can sometimes be misleading when talking about environmental TEM [7] as a particular reaction being induced during an experiment might be desirable in some cases. In this thesis, the term "beam effects" is being used throughout to reflect this.

There are multiple ways in which the electron beam can interact with the sample. Heating occurs when the electron beam transfers energy to the sample in the form of phonons. Whether heating is significant or not depends on the thermal conductivity of the sample. In the case of thermal insulators like polymers, the heating can theoretically be as high as hundreds or thousands of degrees Celsius, whereas metals tend to stay closer to tens of degrees. Radiolysis is another pathway through which the electron beam can change the sample. Electrons that scatter inelastically can transfer their lost energy to breaking chemical bonds in the sample. In purely metallic materials this is not so much of a concern due to the delocalized nature of metallic bonds.

3.2 Environmental transmission electron microscopy

A limitation for conventional TEM is the fact that materials analyzed are synthesized *ex situ*, meaning outside of the system where it is created or used. In order to look at chemical processes or synthesize material in real time, environmental TEM can be used. In an ETEM, the environment of the sample can be manipulated in some way while the sample is being viewed, *in situ*. Different ETEMs exist with different equipment for control of specific environmental parameters, one type uses a gas handling system in conjunction with a heated sample substrate in order to perform metal-organic chemical vapor deposition (MOCVD) for synthesis.

3.2.1 Metal-organic chemical vapor deposition

Metal-organic chemical vapor deposition is a synthesis technique utilizing metal-organic compounds for supplying a metallic element to a substrate. The metal-organic is injected into a high-vacuum chamber in gas form diluted by H_2 , and is then degraded by heating which leaves the metal atom on the substrate.

It is a versatile and common technique in nanofabrication for creating structures such as thin films, nanoparticles and nanowires in a variety of different materials.

The metal-organic "cracking" works by successively releasing methyl radicals until the metal atom is free. The radicals then go on to react with each other and the H₂ carrier gas forming new carbon compounds which hopefully get pumped out by the vacuum system. In reality, it is possible for these compounds to be incorporated into the material or be deposited onto the surface [9].

MOCVD in ETEM has been shown to give insights into the formation processes in synthesis of nanoparticles, and that knowledge of such mechanisms is useful for developments in engineering specific phases or facets for those nanoparticles [10]. ETEM has previously been proposed for the investigation of catalysts for CO₂ hydrogenation *in situ* [11].

One obstacle for ETEM and introducing gas during electron microscopy measurements is the desire to both have a clear ballistic path through the sample for the electron beam, and to contain the gas at a high enough pressure. There are two approaches to this, using either a closed cell or an open cell gas holder. A closed cell holder contains the gas using a top and bottom window made from a thin film. This has the advantage of being able to maintain a higher pressure while sacrificing some image clarity due to the unavoidable overlap of sample and window. An open cell holder does away with the windows for the sake of image clarity while instead sacrificing gas pressure as it is free to escape from the top and bottom of the holder.

When performing *in situ* ETEM experiments, the temperature plays an important role in the results. Not only does it determine the location on the y-axis of the phase diagram, but also the amount of metal-organic that will be cracked. This in turn affects the amount of material available from the precursor, and thus also the location on the x-axis. A third point to keep in mind is that EDS detectors are susceptible to blackbody radiation and can thus produce unreliable results due to thermal radiation or even be damaged if pointed at a sample at too high temperature. For the EDS detector in the ETEM at nCHREM, this limits it to analyzing samples at temperatures below ~600 °C. Temperature can also introduce drift through thermal expansion of the sample substrate which can complicate *in situ* studies where a small part of the sample is often studied over a longer period of time.

3.2.2 Microelectromechanical systems in TEM

Microelectromechanical systems can be used to manipulate materials in various ways under an *in situ* TEM experiment. Heating for the purpose of MOCVD can be done using a MEMS chip acting as both a sample substrate and a heating element. One possible construction can be described as follows: a thin film of SiN_x with micrometer-sized holes is surrounded by a spiral of conductive material through which a current can be passed. The current leads to resistive heating which is conducted through the substrate to the sample. A four-point probe measurement is used to measure the drawn current which gives an indication of heating and chip temperature, however calibration of this is only done on a batch basis. In order to calibrate an individual MEMS chip, an EDS strobe peak measurement can be used. The chip is heated to a specific set temperature while measuring the strobe peak around 0 eV. The amplitude and wavelength of the peak is compared to a known reference measurement, and the set temperature adjusted and measurement redone until the measurement and reference match. This way the set temperature of the chip control system can be correlated with a known real-world temperature. The reference measurement is itself gathered from a sample where for example a known phase transition can give a precise temperature.

3.3 Nickel gallium binary system

The potential use of nickel gallium alloys as a catalyst for the CO₂ hydrogenation was first published by Studt et. al. [6] and Sharafutdinov et.al. [12] in 2014, and discussed a year earlier in the PhD thesis of Sharafutdinov [5]. The group used density functional theory, a computer modeling method which indicated the material system to be promising for low temperature and pressure methanol synthesis, as

well as being made out of cheap, abundant materials [5]. Experimentally, they showed that methanol activity was comparable or higher than conventional Cu/ZnO/Al₂O₃ depending on temperature, and that selectivity for methanol compared to CO was significantly higher for Ni₅Ga₃ at ambient pressure.

The chemical formula for hydrogenation of CO₂ into methanol is shown in equation 1:



This reaction is kinetically limited at lower temperatures and thermodynamically limited at higher temperatures [11], indicating a need for a catalyst at lower temperatures. CO is an unwanted byproduct of methanol synthesis, which is created through the reverse water gas shift reaction when pure CO₂ and H₂ is used [12], shown in equation 2:



The Ni–Ga binary system can take on a number of phases depending on the temperature and the ratio between the two constituents. A binary phase diagram for the system is presented in figure 2, and a few select phases are listed in table 1 along with their respective compositional ranges and crystal structures.

Ni–Ga catalysts have been synthesized using a few different methods including incipient wetness impregnation [12][13][14] (which seems to be the most common due to it being the first reported method), co-condensation–evaporation [15], and co-precipitation which was in one comparison shown to have superior properties and higher activity than catalysts synthesized by other methods [15], indicating there might be room to optimize the catalyst.

Multiple papers have been published discussing the active sites and phases of the system. The seminal paper from 2014 [6] mentions Ni₅Ga₃ (also known as the "delta" or "δ" phase) as the phase with highest yield. Another group has investigated the Ni (211) surface, with and without doping of Ga, both being active sites for the process [16]. Others have reported GaO_x to serve as a promoter for the hydrogenation [14]. The exact mechanisms and active sites have not been determined with certainty [17].

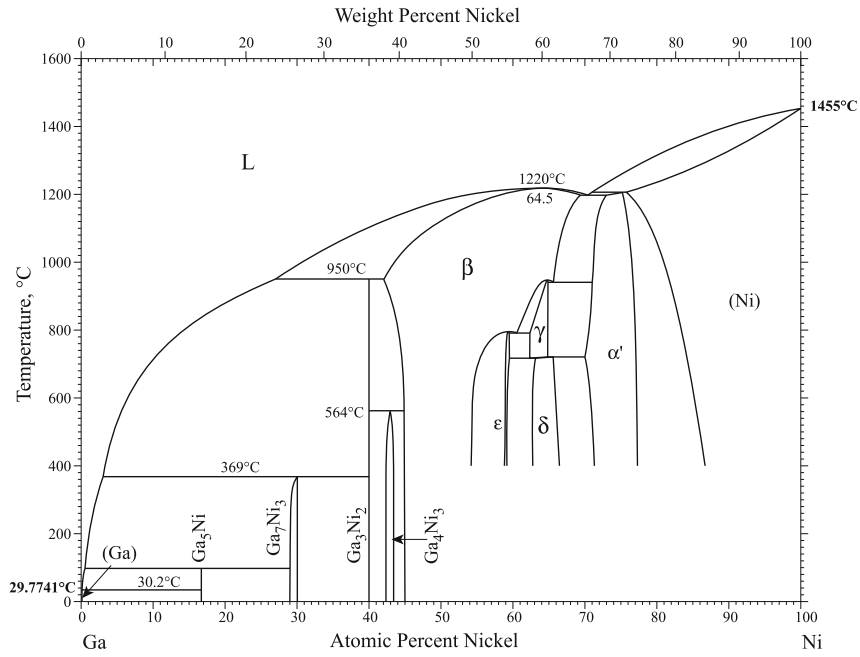


Figure 2: The Ni–Ga binary phase diagram. Used with permission from Springer Nature and retrieved from Okamoto et. al.[18].

Table 1: A few select phases from the Ni–Ga binary phase diagram. Data from Okamoto et. al.[18].

Phase	at.% Ni	Crystal structure
Ni (α)	76-100	Cubic
Ni_3Ga_1 (α')	70-77	Cubic
Ni_5Ga_3 (δ)	63-67	Orthorhombic
$\text{Ni}_{13}\text{Ga}_9$ (ϵ)	59-60	-
Ni_1Ga_1 (β)	42-69	Cubic
Ni_3Ga_4	42-43	Cubic
Ni_2Ga_3	40	Trigonal
Ga	0	Orthorhombic

4 Method

This section lists a few pieces of equipment used, describes some of the preparation of the samples as well as the gas handling system, and finally some of the steps of the analysis and data processing.

The instrument and some aspects of the method were described by Tornberg et. al [19] as well as Hetherington et. al [20]. Some of the method and analysis is inspired by Seifner et. al. [10].

4.1 Equipment used

The TEM used for this study is the Hitachi HF-3300S at the national Center for High Resolution Electron Microscopy (nCHREM) in Lund. This microscope is equipped with:

- a Gatan OneView IS CMOS camera sensor
- a CEOS BCOR spherical aberration correction system

- an Oxford Instruments EDS detector
- an open cell sample holder with support for MEMS chips
- Norcada MEMS chip sample substrates
- a custom MOCVD system described in section 4.4

...and more. A simplified schematic of the microscope can be seen in figure 3a.

4.2 Sample preparation

The MEMS chips carrying the samples are manufactured by Norcada, and consist of a thin SiN_x film with a array of $2\ \mu\text{m}$ holes, all surrounded by a tungsten heating spiral [21]. These chips have a thermal limit of $\sim 1100\ ^\circ\text{C}$, above which they have a tendency to spontaneously break and take the sample with them into the depths of the TEM column. A schematic of a MEMS chip is displayed in figure 3b.

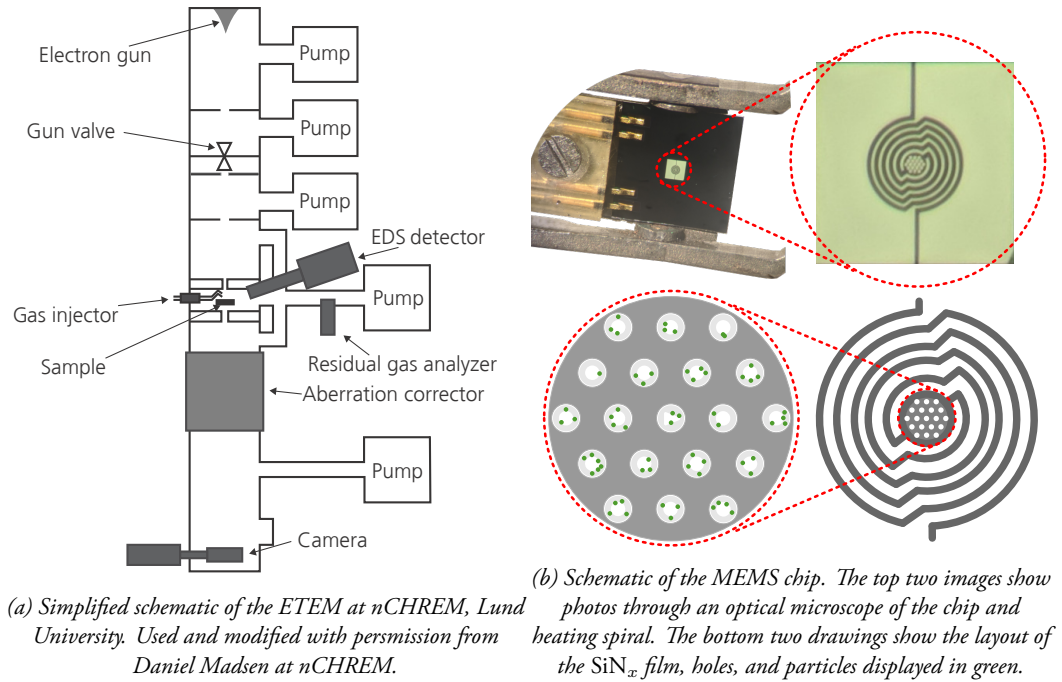


Figure 3: Schematics of the ETEM and MEMS chips.

Two sources of Ni nanoparticles were used. Some experiments were performed using material from Sigma-Aldrich. Others were performed using particles synthesized using spark ablation by Mehran Sedrpooshan at Lund University. These were manufactured with a nominal diameter of 30 nm.

For the commercial nanoparticles, powder was carefully deposited onto MEMS chips, and excess material not adhered to the SiN_x film was removed using a small dust blower. Nanoparticles produced through spark ablation were directly deposited onto MEMS chips as part of the synthesis process. After being loaded into the ETEM, particles were annealed for 10 or 30 min at $700\ ^\circ\text{C}$. This was to reduce the amount of grain boundaries and other defects, which makes subsequent analysis simpler. In some cases, a flow of pure H_2 during annealing was also used in order to reduce any potential contaminant like oxides or carbon deposits on the particles, also to make analysis simpler.

The choice of particle size is an important factor in this type of experiment. Ideally, an electron from the beam should on average only interact once inside the sample to produce the best image quality. In a thicker sample, electrons can interact multiple times and produce effects such as double diffraction, which are much harder to interpret and analyze. The choice of 30 nm is small enough to provide an opportunity for collecting atomic resolution TEM images.

4.3 General experimental procedure

Due to the limited time and number of experiments, the method of when or how to change parameters was not exact. Rapid trial and error was employed to get an overview of the parameter space, with initial values informed by ones used in other projects at the same instrument [10].

During the course of each experiment, different values for temperature, gas concentration and supply were tried. An overarching goal was to observe a pure particle transform from nickel phase to Ni_5Ga_3 , and values were adjusted in accordance with this goal. Precursor supply was usually cut off whenever the currently observed transformation seemed to have stopped visually, or EDS indicated particles contained a high amount of gallium. When possible, complete transformations of single particles were captured in a series of images from pure nickel to a more gallium-rich phase with a constant precursor supply. In other cases, a transformation from one gallium-containing phase to another were captured instead, or individual images of particles after precursor supply had already been stopped.

4.4 Gas handling system

The gas handling system (GHS) is what is responsible for controlling the mixing and flow of gases into the microscope. Most flows in the gas handling system are both measured and controlled using devices called mass flow controllers. Metal-organics are supplied by bubblers, cooled tanks containing the metal organic compound in liquid form. By flowing H_2 into the liquid, the "bubbles" of H_2 emerging from the liquid will carry some of the compound with it. The mix of H_2 and metal-organic is usually further diluted with H_2 in order to get a desired concentration before being injected into the microscope. Any gas that is not sent to the microscope is instead vented into a scrubber system. Any gas removed by the microscope vacuum pumps also eventually reaches the same scrubber system.

By mixing pure H_2 with TMGa in the gas lines, a specific gas composition can be achieved. The total flow of the gas mixture to the sample chamber is also controlled. All flows in the gas handling system are controlled and measured using mass-flow controllers. A schematic of the GHS can be seen in figure 4. CO_2 was supplied using a bottle of dry ice cooled with liquid nitrogen, which is also represented in the schematic. This bottle was not controlled together with the rest of the gas handling system, the inlet was instead adjusted entirely by hand using a manual valve. The concentrations of CO_2 , TMGa, H_2 , and other trace gases in the microscope were measured using a residual gas analyzer, a kind of mass spectrometer that measures the atomic mass of molecules pumped out by the vacuum system.

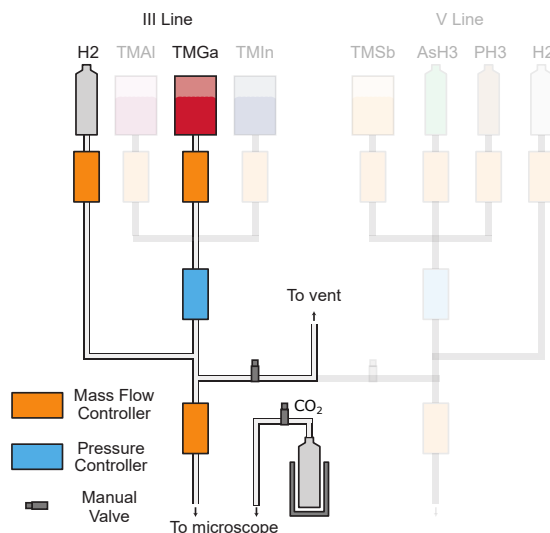


Figure 4: Diagram of the gas handling system. Gas supplies not used in this study are grayed out. Note that the CO_2 source is separate from the rest of the system and is controlled solely by a manual valve. Used and modified with permission by Sjökvist [22].

4.5 Data processing

The ICSD (Inorganic Crystal Structure Database) is a source of .cif (crystallographic information file) structure files from research papers describing the crystal structure of various compounds. Structure files for relevant elements and compounds like Ni, Ni_2Ga_3 , Ni_3Ga , Ni_5Ga_3 , etc... were retrieved from the database. The software SingleCrystal was used to generate simulated diffraction patterns based on retrieved structure files, which were compared with FFTs of micrograph images in order to determine the observed crystal structure. In cases where a nanoparticle is aligned to a higher index direction and only individual planes are visible, the distance between those planes can be measured and compared to distances generated by SingleCrystal. This is less reliable as an overlap of a single interplanar distance between two different phases is more likely than a whole pattern overlapping. More details can be found in appendix C.

For some images, a kind of diffraction filtered image was generated by applying a mask to a pair of spots in the FFT image and performing an inverse FFT. The resulting image shows all the pixels which have contributed to that particular pair of spots. This way, regions with similar crystal structure in a particle can be more easily identified. An image of the contribution from a spot pair can also be overlayed on top of the original, unmasked, image to better indicate the locations of different structures with relation to the rest of the image. In essence, this method produces a similar result to dark field imaging in TEM where an objective aperture is inserted to image only the contribution from a single diffraction spot. FFTs, masking, inverse FFTs and so on were done using DigitalMicrograph.

The GHS reports flows of gases in units of SCCM (standard cubic centimeters per minute, or $\text{cm}^3_{\text{STP}}/\text{min}$) which is a measure of volume per time. Using known parameters and fitting values of the microscope and gases involved, the molar flux (mol/min) of the precursor gas can be calculated. As an example, an output of 200 SCCM H_2 mixed with 7 SCCM TMGa into a flow of 0.6 SCCM to the microscope is calculated to yield a flow of $2.33 \cdot 10^{-8}$ or $23 \text{ nmol}_{\text{TMGa}}/\text{min}$.

5 Results

This section presents the experimental results and analysis from four experimental sessions. Parameters were adjusted multiple times over the course of every experiment, and the presented results are either images after gas supply has been stopped, or a time-series of images during the supply of precursor gas.

Section 5.1 presents a number of images collected after a high flow of 33 to 50 nmol/min TMGa was supplied. For two subsequent experiments, lower flows of 6 nmol_{TMGa}/min and 23 nmol_{TMGa}/min were used, presented in section 5.2 in the form of two time series of images. Synthesized particles were also observed under a flow of CO₂, described in section 5.3.

5.1 High TMGa flow

In the following section, an experiment using a higher flow of TMGa is described.

A flow of 50 nmol/min at 400 °C was supplied for ~30 min, followed by a flow of 33 nmol_{TMGa}/min at 300 °C for ~8 min. Figure 2 shows two nanoparticles after gas flow was stopped, both in realspace images and their respective FFTs. Diffraction patterns for Ni₂Ga₃ in the [210] direction was matched with one, and Ni₂Ga₃ in the [100] direction was matched with the other. Multiple spherical particles were discovered in the vicinity of these particles. EDS results indicated these to consist of close to pure gallium. One of these particles is displayed in figure 5c.

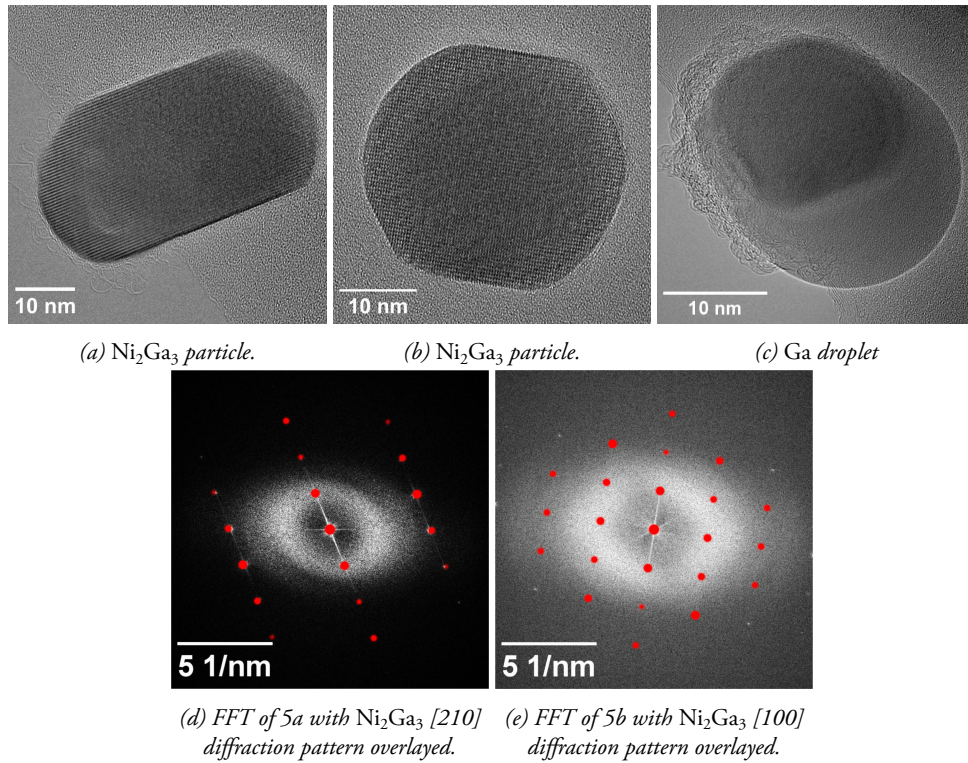


Figure 5: Two nanoparticles synthesized using a high flow of TMGa and their respective FFTs with simulated diffraction patterns overlaid.

Both crystalline particles displayed in figure 5 were also analyzed using EDS. The compositional results of that analysis are displayed in table 2. EDS results alone would place the particles in the Ni₁Ga₁ phase, which does not match with the matched FFT patterns.

Table 2: Chemical composition of particles in figure 5 collected using EDS.

Image	at.% Ni	at.% Ga
5a	47	53
5b	48	52

5.2 Low TMGa flow

In the following section, two experiments with lower flow values and higher temperatures are described.

A flow of 6 nmol_{TMGa}/min was supplied at 400 °C for roughly 30 min, followed by 30 min without gas during which a few particles were analyzed using EDS. These showed results of 66, 76, and 92 at.% Ni. The same flow of gas was supplied again before starting analysis of a particle seemingly consisting of two different regions. The lower left part was shown to consist of 71 at.% Ni, and the upper right part to consist of 79 at.% Ni according to EDS. This particle was observed over the course of ~13 min during which the both the left region and the right region seemed to shrink in favor of a new crystalline region forming on top. A series of images of the process is displayed in figure 6. 6a also shows the rough regions analyzed for EDS circled in blue. EDS was collected after the observation, resulting in a composition of 66 at.% Ni. The compositions are tabulated in table 4.

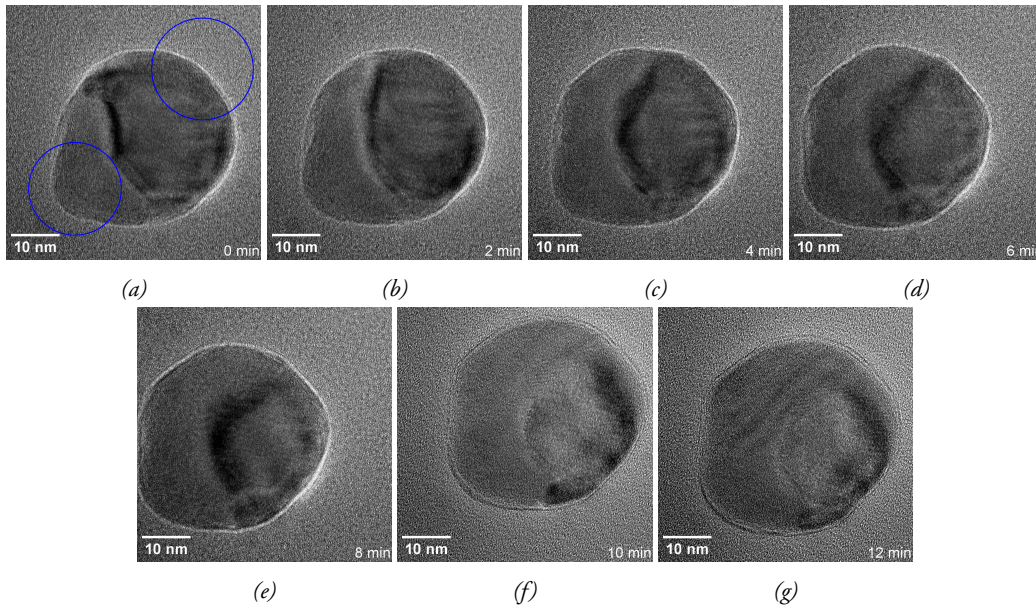


Figure 6: HRTEM images of phase transformation in Ni–Ga nanoparticle under 6 nmol_{TMGa}/min at 400 °C in 2 min intervals. Focus was readjusted for images in 6f and 6g. Blue circles in 6a indicate regions where EDS spectra have been collected.

Table 3: Chemical composition of two particles in figure 5 collected using EDS.

Image	at.% Ni	at.% Ga
6a upper right	79	21
6a lower left	71	29
6g	66	34

The particles before and after recorded transformation were analyzed further using FFT. The FFT at zero

minutes showed only one pair of spots, which were measured to correspond to an interplanar distance of $2.1 \text{ \AA}$ (4.7 nm^{-1}), shown in figure 7a. A filtered image of the contribution from this pair of spots was created and overlaid on top of the original image, shown in figure 7c. The same process was repeated for the image after 12 minutes, where multiple new spot pairs were visible, shown in figure 7b. A second pair of spots was measured to correspond to an interplanar distance of $2.5 \text{ \AA}$ (4.0 nm^{-1}), filtered and overlaid over the original, figure 7d. The second pair of spots was chosen due to the large area contributing to the original image. The lower left region of the particle remained unaligned from beginning to end, giving no clear diffraction spots. The red and green highlighting suggests the particle is heterogeneous after 12 minutes of precursor supply as the original interplanar spacing is still present as well as a new one not present from the start.

An interplanar distance of $2.1 \text{ \AA}$ could be a match with Ni [111] or Ni_3Ga [111] directions. A distance of $2.5 \text{ \AA}$ could match with Ni [110] or Ni_3Ga [110]. Ni and Ni_3Ga having very similar crystal structures is a possible explanation for the ambiguity in the results.

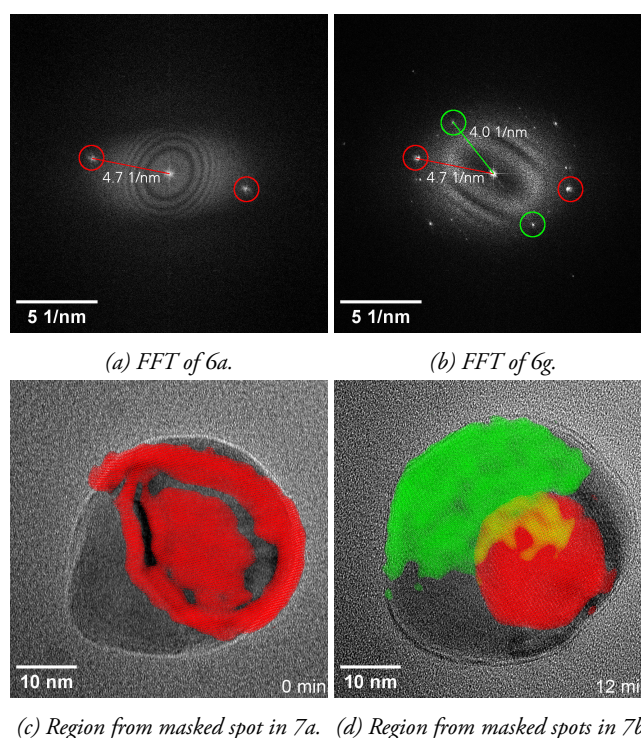


Figure 7: FFTs and highlighted regions of Ni–Ga nanoparticle before and after the transformation displayed in figure 6. Red and green circles in FFTs show the spots used for the respective colored highlights in the realspace images.

In another experiment, flow of $23 \text{ nmol}_{\text{TMGa}}/\text{min}$ was supplied at a temperature of 600°C for approximately 10 min while a continuous movie was recorded, after which the temperature was reduced to 500°C to allow for EDS measurements. HRTEM images spaced 1 min apart are shown in figure 8. Growth in the first minute is concentrated to the flatter faces in the top left and the right of the particle. The second and third minute shows continued growth along the top and top left. Minute 4, 5, and 6 showed the most growth in the left side of the particle. Moiré-like fringes indicating strain develop in the left side of the particle from minute 1 and onwards, before partly disappearing by minute 5 and being mostly gone by minute 6. The bottom edge of the particle, which is covered in what could be graphite layers from before gas was supplied, did not see any visible growth.

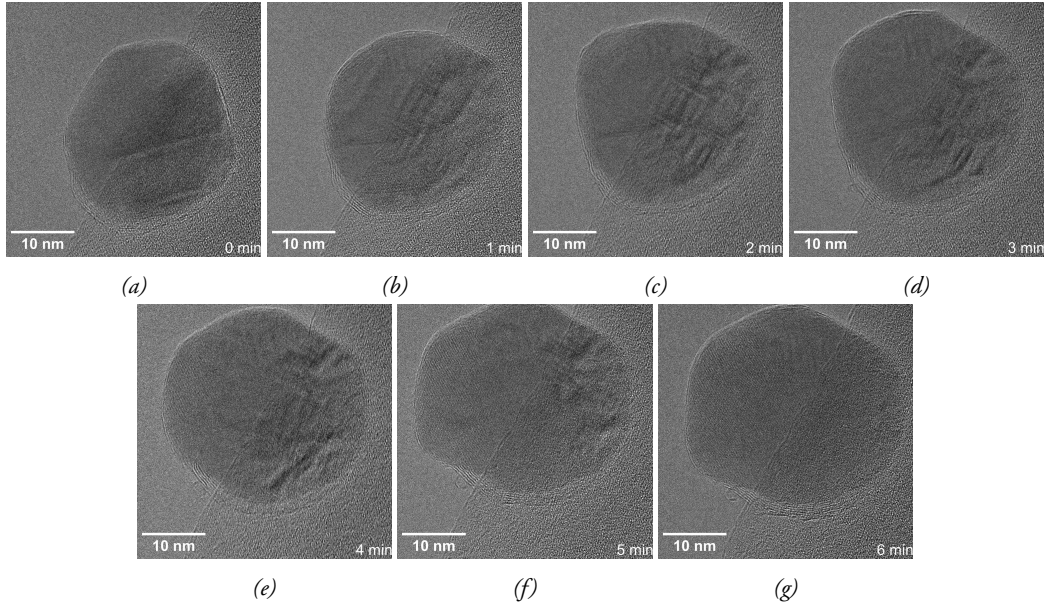


Figure 8: HRTEM images of phase transformation of Ni nanoparticle to Ni–Ga alloy under $23 \text{ nmol}_{\text{TMGa}}/\text{min}$ at 600°C in 1 min intervals from the moment gas supply was started (figure 8a), up until the 6 minute mark when transformation had stopped (figure 8g).

EDS spectra for the particle were collected just before gas supply started, and 10 min later when the gas supplied and temperature was lowered back down to 500°C . The results indicated the pre-transformation particle to be within the Ni solid solution phase, and the post-transformation particle to be approximately 57 at.% Ni to 43 at.% Ga. Exact EDS compositions are shown in table 4.

Table 4: EDS composition before and after $23 \text{ nmol}_{\text{TMGa}}/\text{min}$ at 600°C for 10 min.

Time	at.% Ni	at.% Ga
0 min	94	6
10 min	57	43

FFT of figures 8a and 8g were both compared with possible crystal structures. The particle at 0 min matched with the simulated diffraction pattern of pure Ni in the $[100]$ direction, shown in figure 9c. The particle at 12 min had a more complex pattern, which was matched with two sets of Ni_5Ga_3 $[100]$ patterns with a rotation of $\sim 120^\circ$ with respect to each other and with absences displayed, which is shown in figure 9d. The patterns without overlays can be seen in figures 9a and 9b.

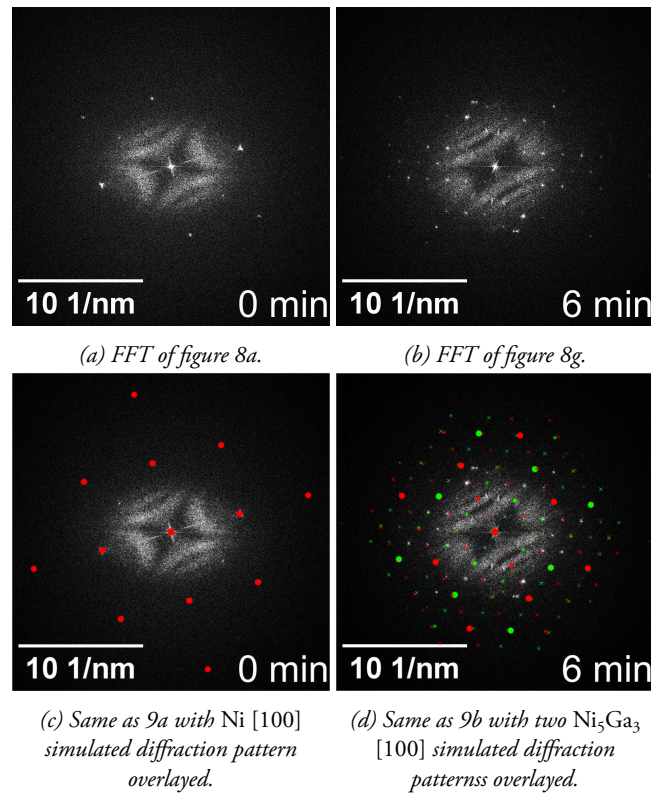


Figure 9: FFTs and matching simulated diffraction patterns of Ni nanoparticle before and after exposure to 23 nmol_{TMGa}/min at 600 °C for 6 min.

A sample of six particles not under the beam were analyzed using EDS after the transformation displayed in figure 9 and after gas supply had been shut off. These ranged in composition from 80 at.% Ni to 56 at.% Ni. The composition distribution of these particles is shown in figure 10.

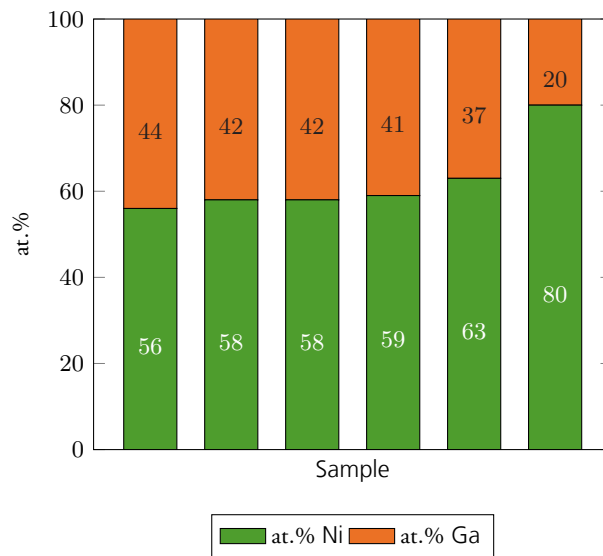


Figure 10: Composition of random sample of particles according to EDS after 23 nmol_{TMGa}/min was supplied for 10 min at 600 °C without the electron beam.

5.3 Observation with CO₂

This section describes an experiment where synthesized Ni–Ga were observed while supplying CO₂ to the column.

One experiment focused on observing synthesized particles under an atmosphere of CO₂ and H₂. Before any gases had been introduced to the system, oxidation was observed on the Ni nanoparticles. This is believed to stem from the newly connected gas lines for adding CO₂. Oxidation was likely reduced when supplying H₂.

Ni–Ga synthesis was attempted using 23 nmol_{TMGa}/min at 600 °C. The synthesis was complicated by the presence of oxygen mentioned as well as some contamination by antimony (Sb), which is another metal frequently used in the ETEM. After ~2 h, a few particles had incorporated around 20 at.% Ga and the experiment proceeded to activation. Activation of particles was attempted using $1.3 \cdot 10^{-4}$ mol/min H₂ at 600 °C for 1 h inspired by the activation process described in Zimmerli et. al.[17]. CO₂ was supplied and detected by the residual gas analyzer. The oxygen content of observed particles increased significantly, upwards of 80 at.% according to EDS, although the plausibility or implications of this very high oxygen signal was not explored in depth.

6 Discussion

This section discusses the results of the thesis, their implications, and some improvements and considerations for future studies.

6.1 Phase and facet engineering

Due to time constraints, the availability as well as the time consuming nature of the instrument, only a handful of parameter combinations were tested, and the ones that were tested have a sample size of one or two. Nevertheless, qualitatively this still gives a lot of results to go on. It was shown that Ni–Ga nanoparticles can be synthesized using Ni nanoparticles and TMGa, and that some control over the phase of these particles can be exerted using temperature and precursor supply. Using TMGa flows of 50 to 33 nmol_{TMGa}/min at a temperature switching from 400 and 300 °C yielded a composition richer in Ga and what is believed to be Ni₂Ga₃. Using a flow of 6 nmol_{TMGa}/min at 400 °C yielded a composition closer to 3:2 Ni:Ga, but a specific phase could not be determined. A flow of 23 nmol_{TMGa}/min at 600 °C yielded a composition 57:43 and a suspected phase of Ni₅Ga₃. The rate of transformation between 6 and 23 nmol_{TMGa}/min at 400 and 600 °C respectively was also shown to be much different. The lower particle under lower flow was shown taking 12 min to go from roughly 75 to 66 at.% Ni, and the second (presumably) taking around 6 min to go from 94 to 57 at.% Ni (as that is the time at which the particle had stopped changing visually). More work is needed to decouple the effect of raising the temperature and raising the amount of TMGa flow.

The results of figure 10 indicate that all of the Ni particles do not acquire the same exact composition after the same temperature and gas flow conditions. It is possible that different sizes of the particles and levels of contamination on the surface (like the suspected carbon layers seen in figure 8) affected the rate of the transformation, and that all the particles could have ended up with the same thermodynamically favored composition eventually if gas supply was continued.

Previous research has indicated that the [221], [111] faces of Ni₅Ga₃ particles are most important for CO₂ hydrogenation [23]. One point of interest for future studies would be to observe which facets are most favored during synthesis, and if the faces can be engineered in some way. Maximizing the relative sizes of the most active facets is a way one could improve the catalytic activity of the material. The facets of the Ni₂Ga₃ particles shown in figure 5 indicate these might be energetically favored during growth under the conditions used. The flat top and sharp corner of the particle visible in figure 6g is likely an example of the same thing.

The two overlapping and rotated diffraction patterns from the same crystal viewing direction needed to form the FFT shown in figure 9b could be explained by twinning. Twinning is a crystal defect occurring in crystals sometimes described as a mirroring of atomic layer stacking in a plane. Twinning and other defects can positively or negatively affect both the stability and the activity of nanocatalysts [24], which could warrant further investigation into the phenomenon.

The difficulty in specifying the phases present in figure 6 stems from three problems. The first is that composition did not start out at 100 at.% Ni. The second is the multiple regions present, which can give the FFT multiple overlapping patterns which are much harder to analyze. The final problem is the fact that the distances of 2.1 Å and 2.5 Å both correspond quite well to distances present in both pure Ni and Ni₃Ga. These phases are both cubic with a very similar lattice parameter (), making them difficult to distinguish from each other just from diffraction of FFT.

6.2 Beam effects

The electron beam is suspected to have influenced the transformation of nanoparticles at multiple points during the experiments. At times, a particle observed over a longer time was seen incorporating a significant amount of Ga, and particles analyzed afterwards seemed to have a significantly lower Ga content. A weak indication of this is the composition of a particles under the beam shown in table 4 compared with the particles not under the beam shown in figure 10. A more comprehensive statistical analysis would have to be done to definitively say that the beam influenced the transformation.

A phase change without the electron beam would be preferable if one would want to study or scale up the process in *ex situ* MOCVD. Potential beam sensitivity could however provide an easier environment to study the transformation itself *in situ*. If a condition is found where Ni particles stay mostly pure only until the electron beam is introduced, the reaction can easily be studied multiple times per sample in quick succession. Perhaps one should think about if the reaction takes the same pathway in both the scenario with electron beam and with elevated temperature.

The exact mechanism responsible for the electron beam sensitivity of different materials and reactions is not always clear. Williams & Carter claim that metals (and thus presumably intermetallics) have a negligible heating due to the electron beam [7]. Radiolysis is also claimed to have a relatively weak impact on metals due to the bonds being delocalized. Radiolysis could perhaps contribute to cracking of TMGa, although as Tornberg et. al. have shown, the fraction of gas that interacts with the electron beam that interacts with the electron beam is very small [19] suggesting this would not have a large impact on the reaction dynamics of a growth experiment.

6.3 Contamination

The microscope used is equipped with a pressure gauge inside the column close to the sample. This gauge can be calibrated to give the total gas pressure at the sample which can further be used to calculate the relevant partial pressures of gas TMGa for example. Partial pressures can be argued are a better metric to report than moles per minute as the partial pressure also takes into account the rate at which the gas leaves the sample which is dependent on the surrounding geometry. During experiments where the pressure gauge was turned on (the gauge was not turned on in the experiments represented in the results section), particles contaminated with arsenic was discovered within the sample which were not present during experiments where the gauge was turned off, leading us to believe the arsenic was coming from the gauge itself. Other researchers using the same equipment are using an arsenic-containing hydride for their experiments, which would explain the presence of arsenic. Images of the accidental nickel arsenide particles can be seen in appendix A. In an failed experiment not discussed in this thesis due to the TMGa bubbler being empty, contamination of antimony was also detected. This element is also used in the same microscope, in the form of trimethylantimony.

The phenomenon of finding unwanted gases stemming from previous sessions in MOCVD is often called

the memory effect, and is more prevalent with some gases than others. A common way to combat this effect is to flush the system one or multiple times with an inert gas like hydrogen or nitrogen in the hope of getting rid of any residues.

The source for CO₂ seemed to be heavily contaminated by O₂. These contaminants were present even before opening the valve for the dry ice bottle itself, indicating the contaminants might be stemming from the extra piping and fittings attaching the bottle to the microscope inlet. The dry ice used was not necessarily pure either. For future studies of these type of catalysts under active conditions, a more precise supply of CO₂ should be used. This can not only be beneficial in the elimination of contaminants, but also the precise control of flows for the sake of reproducibility. The ratio of H₂ and CO₂ is also a parameter for optimal use of different catalysts [11]. The system is limited in the total pressure possible before an automatic shutdown is triggered to protect the electron gun. This could be a problem if effects of CO₂ are only apparent near ambient pressures. In this case, the system would perhaps not be suitable for a study under CO₂.

6.4 Possible shortcomings and improvements

The results presented do not account for the amount of H₂ entering the column. The reported flows of TMGa are calculated from the dilution and the total amount of gas flowing into the column, but the ratio of H₂ to TMGa can vary between experiments. Hydrogen might be responsible for reducing any potential GaO_x starting to form. Previous research suggests that the interface between a Ni–Ga and GaO_x plays a role in the selectivity of the catalysis [17]. A further development of this study could be to determine the presence of a Ni-free outer layer on synthesized particles using EDS in scanning transmission electron microscopy, or STEM-EDS. This would be able to give spatially resolved chemical composition of the sample. This assumes the oxide is thick enough to be visible despite the excitation volume size of the electron beam, which is a limiting factor in the resolution of STEM-EDS. If enough oxygen is present, like in experiments conducted by Gallo et. al, [14], the oxide should be clearly visible in TEM. In any case, STEM-EDS could be useful for more accurately determining the composition differences between regions of single particles, such as those seen in figure 6. If no GaO_x is found to be present due to the presumed reducing effect of H₂, a controlled flow of O₂ into the microscope might be worth a consideration.

One proposed method for recording composition change during transformation was to take intermittent EDS spectra as the transformation is happening. This would limit observation at temperatures below 600 °C, and a trade-off of counts vs. time resolution would have to be considered. Perhaps some idea of the trend of the composition could be gleaned with this method at least.

7 Conclusions and outlook

Synthesis of specific phases of Ni–Ga alloy nanoparticles using Ni nanoparticles and TMGa was shown to be possible *in situ* in ETEM with MOCVD. Although only a very small section of the parameter space has been explored, it is clear that the temperature and amount of supplied TMGa affected the rate of transformation and resulting phase of the synthesis. This is a good indication for future studies of the same material system *in situ*, where more definitive insights into the dynamics of formation can hopefully be found.

While exposure to CO₂ did not provide any notable insights into the catalytic reaction or the behavior of the particles, experiments in the future might benefit from a more controlled source of the gas, preferably utilizing a mass-flow controller like other sources present in the GHS. This could improve reproducibility and allow for better control over the course of an experiment. Still, equipment like the ETEM might be used more appropriately in other ways than observing the hydrogenation reaction itself, not least due to the limited total pressure possible. A controlled source of O₂ might also be interesting for studying GaO_x in the context of Ni–Ga catalysts.

Other materials like gallium nitride (GaN) has been shown to convert methanol to ethanol and higher alcohols via photocatalysis [25], and nickel arsenide, nickel antimony, have been shown to catalyze the splitting of water into hydrogen and oxygen [26][27]. Seeing as these materials have related applications to Ni–Ga catalysts, they might benefit from the same type of *in situ* synthesis studies.

8 References

- [1] IPCC. “Summary for Policymakers”. In: *Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Ed. by Core Writing Team, H. Lee, and J. Romero. Geneva, Switzerland: IPCC, 2023, pp. 1–34. DOI: 10.59327/IPCC/AR6-9789291691647.001.
- [2] International Energy Agency. *Net Zero by 2050*. Paris: IEA, 2021. URL: <https://www.iea.org/reports/net-zero-by-2050>.
- [3] Hannah Ritchie, Pablo Rosado, and Max Roser. “Greenhouse gas emissions”. In: *Our World in Data* (Jan. 5, 2024). URL: <https://ourworldindata.org/greenhouse-gas-emissions> (visited on 05/03/2024).
- [4] Trinath Biswal et al. “Conversion of carbon dioxide to methanol: A comprehensive review”. In: *Chemosphere* 298 (2022), p. 134299. ISSN: 0045-6535. DOI: <https://doi.org/10.1016/j.chemosphere.2022.134299>. URL: <https://www.sciencedirect.com/science/article/pii/S0045653522007925>.
- [5] Irek Sharafutdinov. “Investigations into low pressure methanol synthesis”. PhD thesis. Department of Physics, Technical University of Denmark, 2013.
- [6] Felix Studt et al. “Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol”. In: *Nature Chemistry* 6.4 (Apr. 1, 2014), pp. 320–324. ISSN: 1755-4349. DOI: 10.1038/nchem.1873. URL: <https://doi.org/10.1038/nchem.1873>.
- [7] David B. Williams and C. Barry Carter. *Transmission Electron Microscopy*. Publication Title: Springer-Link. Springer US, 2009. ISBN: 978-0-387-76501-3. URL: <https://link.springer.com/book/10.1007/978-0-387-76501-3>.
- [8] M. Ek, Sebastian Lehmann, and Reine Wallenberg. “Electron channelling: challenges and opportunities for compositional analysis of nanowires by TEM”. In: *Nanotechnology* 31.36 (June 2020). Publisher: IOP Publishing, p. 364005. DOI: 10.1088/1361-6528/ab9679. URL: <https://dx.doi.org/10.1088/1361-6528/ab9679>.
- [9] Örjan Danielsson et al. “A model for carbon incorporation from trimethyl gallium in chemical vapor deposition of gallium nitride”. In: *J. Mater. Chem. C* 4 (Jan. 2015). DOI: 10.1039/C5TC03989D.
- [10] Michael S. Seifner et al. “Insights into the Synthesis Mechanisms of Ag-Cu₃P-GaP Multicomponent Nanoparticles”. In: *ACS Nano* 17.8 (2023), pp. 7674–7684. DOI: 10.1021/acsnano.3c00140. URL: <https://doi.org/10.1021/acsnano.3c00140>.
- [11] Marc D Porosoff, Binhang Yan, and Jingguang G Chen. “Catalytic reduction of CO₂ by H₂ for synthesis of CO, methanol and hydrocarbons: challenges and opportunities”. In: *Energy & Environmental Science* 9.1 (2016). Publisher: Royal Society of Chemistry, pp. 62–73.
- [12] Irek Sharafutdinov et al. “Intermetallic compounds of Ni and Ga as catalysts for the synthesis of methanol”. In: *Journal of Catalysis* 320 (2014), pp. 77–88. ISSN: 0021-9517. DOI: <https://doi.org/10.1016/j.jcat.2014.09.025>. URL: <https://www.sciencedirect.com/science/article/pii/S0021951714002760>.
- [13] Daniel A. Torelli et al. “Nickel–Gallium–Catalyzed Electrochemical Reduction of CO₂ to Highly Reduced Products at Low Overpotentials”. In: *ACS Catalysis* 6.3 (2016), pp. 2100–2104. DOI: 10.1021/acscatal.5b02888. URL: <https://doi.org/10.1021/acscatal.5b02888>.
- [14] Alessandro Gallo et al. “Ni₅Ga₃ catalysts for CO₂ reduction to methanol: Exploring the role of Ga surface oxidation/reduction on catalytic activity”. In: *Applied Catalysis B: Environmental* 267 (2020), p. 118369. ISSN: 0926-3373. DOI: <https://doi.org/10.1016/j.apcatb.2019.118369>. URL: <https://www.sciencedirect.com/science/article/pii/S0926337319311154>.
- [15] Kaisar Ahmad and Sreedevi Upadhyayula. “Conversion of the greenhouse gas CO₂ to methanol over supported intermetallic Ga–Ni catalysts at atmospheric pressure: thermodynamic modeling and experimental study”. In: *Sustainable Energy Fuels* 3.9 (2019). Publisher: The Royal Society of Chemistry, pp. 2509–2520. DOI: 10.1039/C9SE00165D. URL: <http://dx.doi.org/10.1039/C9SE00165D>.

- [16] Qingli Tang et al. "A new and different insight into the promotion mechanisms of Ga for the hydrogenation of carbon dioxide to methanol over a Ga-doped Ni(211) bimetallic catalyst". In: *Nanoscale* 11.20 (2019). Publisher: The Royal Society of Chemistry, pp. 9969–9979. doi: 10.1039/C9NR01245A. URL: <http://dx.doi.org/10.1039/C9NR01245A>.
- [17] Nora K. Zimmerli et al. "Structure and Role of a Ga-Promoter in Ni-Based Catalysts for the Selective Hydrogenation of CO₂ to Methanol". In: *JACS Au* 4.1 (2024). _eprint: <https://doi.org/10.1021/jacsau.3c00677>. doi: 10.1021/jacsau.3c00677. URL: <https://doi.org/10.1021/jacsau.3c00677>.
- [18] H. Okamoto. "Ga-Ni (Gallium-Nickel)". In: *Journal of Phase Equilibria and Diffusion* 31.6 (Dec. 1, 2010), pp. 575–576. ISSN: 1863-7345. doi: 10.1007/s11669-010-9785-6. URL: <https://doi.org/10.1007/s11669-010-9785-6>.
- [19] Marcus Tornberg et al. "Enabling In Situ Studies of Metal-Organic Chemical Vapor Deposition in a Transmission Electron Microscope". In: *Microscopy and Microanalysis* 28.5 (Oct. 2022), pp. 1484–1492. ISSN: 1431-9276. doi: 10.1017/S1431927622000769. URL: <https://doi.org/10.1017/S1431927622000769>.
- [20] Crispin Hetherington et al. "In situ metal-organic chemical vapour deposition growth of III–V semiconductor nanowires in the Lund environmental transmission electron microscope". In: *Semiconductor Science and Technology* 35.3 (Feb. 2020). Publisher: IOP Publishing, p. 034004. doi: 10.1088/1361-6641/ab6bfd. URL: <https://dx.doi.org/10.1088/1361-6641/ab6bfd>.
- [21] Jane Y. Howe et al. "In situ Thermal Shock of Lunar and Planetary Materials Using A Newly Developed MEMS Heating Holder in A STEM/SEM". In: *Microscopy and Microanalysis* 23 (S1 2017), pp. 66–67. doi: 10.1017/S1431927617001015.
- [22] Robin Sjökvist. "In-situ Study of the Growth, Composition and Morphology of III-V Semiconductor Nanowires". ISBN: 9789174229745 9789174229752. thesis/doccomp. Lund University, 2023. URL: <http://lup.lub.lu.se/record/62031787-1733-4c53-9342-cafb5235e159> (visited on 05/08/2024).
- [23] Huanyu Zhou et al. "Relationship between Structural Properties of the Unsupported Ni₅Ga₃ Catalyst and Methanol Synthesis Activity". In: *Industrial & Engineering Chemistry Research* 63.16 (Apr. 24, 2024). Publisher: American Chemical Society, pp. 6974–6984. ISSN: 0888-5885. doi: 10.1021/acs.iecr.4c00241. URL: <https://doi.org/10.1021/acs.iecr.4c00241>.
- [24] Yang Luo and Yinghong Wu. "Defect Engineering of Nanomaterials for Catalysis". In: *Nanomaterials (Basel)* 13.6 (Mar. 2023). Place: Switzerland.
- [25] Mingxin Liu et al. "Direct Catalytic Methanol-to-Ethanol Photo-conversion via Methyl Carbene". In: *Chem* 5.4 (2019), pp. 858–867. ISSN: 2451-9294. doi: <https://doi.org/10.1016/j.chempr.2019.01.005>. URL: <https://www.sciencedirect.com/science/article/pii/S2451929419300294>.
- [26] Fulvio Bellato et al. "Colloidal Synthesis of Nickel Arsenide Nanocrystals for Electrochemical Water Splitting". In: *ACS Applied Energy Materials* 6.1 (2023), pp. 151–159. doi: 10.1021/acsaem.2c02698. URL: <https://doi.org/10.1021/acsaem.2c02698>.
- [27] Pengyan Xue et al. "First-principles study of the electronic and catalytic properties of nickel-antimony (Ni-Sb) alloy catalyst for hydrogen evolution reaction". In: *Computational Materials Science* 234 (2024), p. 112778. ISSN: 0927-0256. doi: <https://doi.org/10.1016/j.commatsci.2023.112778>. URL: <https://www.sciencedirect.com/science/article/pii/S0927025623007723>.

Appendix A: Nickel arsenide particles

Nickel arsenide (Ni–As) particles observed during Ni–Ga synthesis experiments. The arsenic is believed to have emanated from the pressure gauge connected to the column close to the sample which has been used in other experiments where arsine (AsH_3) is used. The hexagonal shape has been observed in NiAs crystals before, and EDS confirmed the crystals contained both Ni and As. Interestingly, NiAs has been proposed as a catalyst for producing green H_2 through the hydrogen evolution reaction (HER) [26], which would complement Ni–Ga catalysts quite well as green hydrogen is a prerequisite for carbon neutral or carbon negative methanol production.

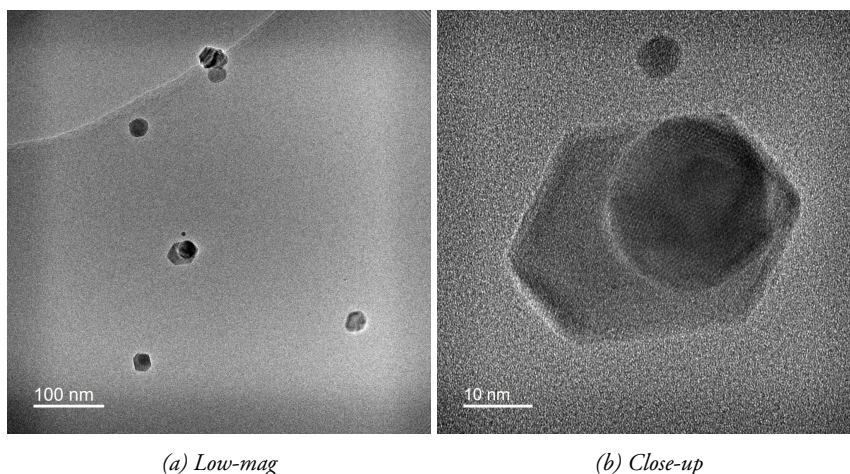


Figure A1: NiAs nanoparticles observed forming from Ni nanoparticles and AsH_3 contaminants.

Appendix B: Dose comparison between aperture sizes

Different condenser apertures inserted at the top of the TEM column affect how many electrons reach the sample. A more narrow aperture could potentially reduce the effective electron dose and thus reduce various beam effects while sacrificing some total brightness in the image. The following is a comparison of the electron dose under conditions typical for HRTEM imaging versus under TEM-EDS. A comparison was made between two apertures, 300 μm and 100 μm to see what affect they had on the dose. Note that the reported doses are not what the particles themselves receive, but the dose of electrons transmitted through the sample and reaching the image sensor. This should be linearly correlated with the amount of electrons interacting with the sample in any given area, and the comparison was done using the same particle for both 300 μm and the narrower 100 μm . The beam was also more condensed using the narrower aperture, making this comparison more qualitative than quantitative.

Figure A2 shows the images used for dose comparison, circles highlighting the regions of interest (ROI) where electrons were counted. The area was cropped in order to attempt to give a representative value for the dose applied to a particle rather than the dose through vacuum or through SiN_x film.

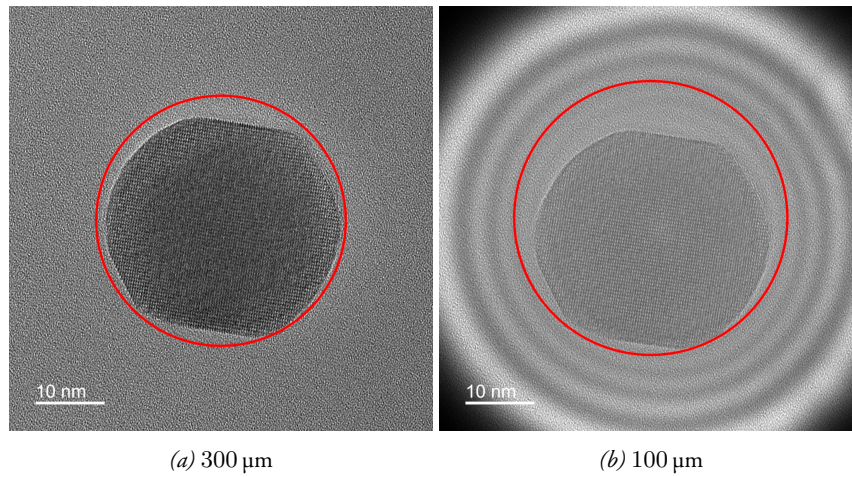


Figure A2: Comparison between two sizes of aperture. The red circles indicate the ROI where electron dose has been calculated. The beam is more condensed in the image with the smaller aperture.

Table A1 shows total electrons counted in the regions of interest highlighted in figure A2 as well as calculated electron doses (given in $\#e^-/\text{\AA}^2\text{s}$ or electrons per square Angström per second) for those same ROI.

Table A1: Total number of electrons and electron doses in the ROI in images shown in figure A2. Electron doses are given in number of electrons per square Angström per second.

Aperture size	Total in ROI [$\#e^-$]	Dose [$\#e^-/\text{\AA}^2\text{s}$]
300 μm	$2.347 \cdot 10^8$	4468
100 μm	$2.100 \cdot 10^8$	3520

This is useful to know for isolating the EDS spectrum of a small part of a sample. The area responsible for the spectrum can be narrowed by condensing the beam which increases the electron dose, which in turn can increase X-ray counts but also be detrimental to the sample stability. The results in table A1 and figure A2 show that the electron beam can be narrowed to a small particle while keeping a similar dose.

Appendix C: Matching crystal structures

This appendix gives additional detail on how some of the data processing methods used in this thesis are performed. In order to match a crystal structure observed in HRTEM to that of a theoretical compound, first, the FFT of the image is generated. Digital Micrograph has a simple function to do just this. The brightness, contrast, and gamma of the resulting image are adjusted so that spots are as clear as possible. Lowering gamma from 50 to 25 is often a good start. The image is then exported to a format that can be read by SingleCrystal, TIF, PNG or JPEG. For the simulated diffraction pattern, a candidate .cif is acquired from the ICSD. EDS can give a good indication for what compounds to try. In SingleCrystal, the .cif and the FFT are loaded and overlayed. The scale of the FFT image must be calibrated using a scale bar overlayed in Digital Micrograph, or by using the width of the image and the ruler tool in SingleCrystal. Different viewing directions and rotations around the viewing axis are tried until a match is found, or it becomes clear there is no match to be made. A diagram of the method is shown in figure A3.

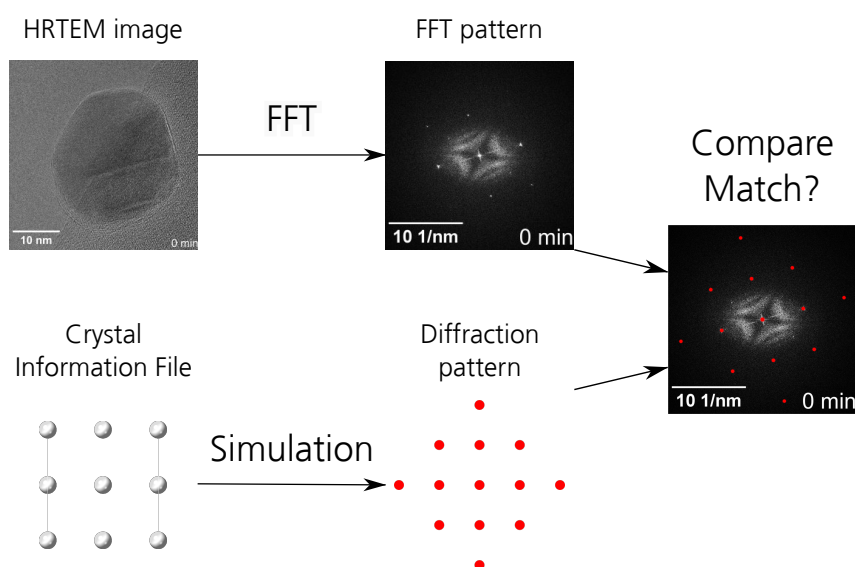


Figure A3: Diagram of the general method for matching an HRTEM image with a specific compound.