1 Introduction

The last two years were marked by two major anniversaries for the field of superconductivity. In 2011 the centenary of the discovery of superconductivity [1] was celebrated at numerous events and conferences, of which the Superconductivity Centennial Conference in The Hague, The Netherlands was one of the most prominent. The following year saw the 50th anniversary of the theoretical prediction of the Josephson effect [2] which was also commemorated at multiple gatherings with the Applied Superconductivity Conference in Portland, Oregon being a major one. Both discoveries paved the way for the study of new physical effects and the development of numerous unique applications and devices. During these five decades the Josephson effect became the basis for almost all superconducting electronics circuits.

Superconductivity and Josephson junctions proved to be very successful for various applications requiring high precision or high sensitivity. For example, superconducting detectors enable the measurement of very weak signals. The most familiar type of these detectors are SQUIDS, **s**uperconducting **qu**antum **i**nterference **d**evices which are currently the most sensitive sensors for weak magnetic fields [3]. In metrology, Josephson junctions have been established as primary standards for the unit of the electrical voltage, the volt, due to the steps of constant voltage they show under microwave irradiation [4].

Since a single Josephson junction can generate voltages of a few millivolts at most, a high number of junctions is connected in series arrays to raise the output voltage to the relevant levels of 1 V or 10 V [5][6]. The fabrication of arrays with a high number of Josephson junctions was found to be a challenge for the existing thin film technology as the properties of every junction have to fit in a margin of suitable values. This challenge was first overcome with strongly underdamped Josephson junctions [7][8]. The hysteretic current-voltage characteristic of this junction type causes overlapping steps of constant voltage under microwave irradiation. Arrays of these strongly underdamped junctions are more tolerant of variations of the parameters of their junctions than arrays of overdamped junctions. Thus underdamped SIS junctions (S: superconductor, I: insulator) became widely adopted for the use in arrays for DC voltage standards. The later implementations of these SIS junctions were fabricated using a barrier of thermally oxidised aluminium between two niobium electrodes. This Nb-Al-AlO_x

technology was developed in the 1980s [9] and is now the mainstay of Josephson electronics. Complete calibration systems for DC voltages based on circuits fabricated using this technology are commercially available from two companies: Supracon, Germany [10] and Hypres, USA [11].
Despite their high, quantum-based accuracy, the usability of voltage standards based on underdamped junctions is limited due to overlapping steps of constant voltage caused by the hysteretic current-voltage characteristic [5]. This ambiguity leads to semi-stable steps and effectively prevents the fast selection of a particular step. Therefore voltage standards based on underdamped Josephson junctions are restricted to DC applications. To overcome these drawbacks and to open additional application fields, junctions with non-hysteretic current-voltage characteristic were investigated. These overdamped junctions provide intrinsically stable constant-voltage steps which can be easily selected by changing the bias current [12]. The first implementation of this programmable Josephson voltage standard was fabricated using externally shunted SIS junctions. But to increase the junction number and thus the output voltage, intrinsically shunted junctions had to be used.
A straightforward way to provide an intrinsic shunt is to replace the insulating barrier with a metallic one. But the resulting SNS junctions (S: superconductor, N: normal metal) suffer from a reduced characteristic voltage due to a low normal state resistance of the metallic barrier. The necessary reduction of the drive frequency requires an increase of the junction number, further complicating the circuit fabrication. SINIS junctions combine the advantages of both the SIS and the SNS type. Two very thin aluminium oxide films separated by a layer of aluminium provide a suitably high characteristic voltage while maintaining an overdamped current-voltage characteristic. After a proof of principle 10 V circuit in 2000 [13], SINIS junctions were the basis of PTB's programmable Josephson voltage standard for operation at 70 GHz for many years. This work culminated into the successful demonstration of the first fully operational programmable 10 V circuit [14]. During this work it was found that the two very thin oxide layers of SINIS junctions are very fragile which caused a low fabrication yield [15].
Aiming to overcome the low characteristic voltage of SNS junctions, experiments with silicide-based junction barriers at NIST [16] lead to the rediscovery of Nb_xSi_{1-x} as a junction barrier material [17]. The first results on Josephson junctions with this barrier were published in 1987 [18]. Nb_xSi_{1-x} films offer two degrees of freedom to tune the electrical parameters of the junction: composition x and thickness d. Therefore characteristic voltage and critical current density can be set almost independently of each other. Thus Josephson junctions with Nb_xSi_{1-x} barriers can

be adjusted to be overdamped and to have a high characteristic voltage. That enables these junctions to be used in a wide range of cryoelectronic applications.

During a successful cooperation between PTB and NIST the first 1 V and 10 V programmable Josephson voltage standards based on Nb_xSi_{1-x} junctions for the operation at 70 GHz were fabricated at PTB [15]. The PTB group aimed to increase the yield of the voltage standard fabrication which was unsatisfactory with the previously used SINIS technology especially for 10 V circuits. After the resounding success of this cooperation the PTB group decided to switch to a technology based on Josephson junctions with Nb_xSi_{1-x} barriers for the fabrication of its AC voltage standards. The implementation of this technology was the first goal of the present work. To accomplish this objective, the deposition parameters of a new co-sputtering system had to be optimised to match the parameter sets required by PTB's AC voltage standards.

In the second part of the present work Josephson junctions with the target parameters were studied to shed light on their remarkable physical properties. It is known that Nb_xSi_{1-x} exhibits a metal-insulator transition [19][20] at which the electrical transport properties change significantly. Previous studies suggest that the target composition for the programmable Josephson voltage standard is close to this transition [17]. If this is indeed the case, small changes in the barrier composition can lead to significant changes in the junction parameters. The junction type also remains to be clarified. Although previously published data suggests SNS-like overdamped behaviour, another study obtained high values for the junction capacitance [21]. This would be highly unusual for SNS junctions as a metallic barrier prevents any charging of the electrodes.

The present work aims to characterise Josephson junctions with Nb_xSi_{1-x} barriers by analysing several junction properties measured on junctions with two different parameter sets which are typical for the two operation ranges at 70 GHz and 15 GHz. To take the metal-insulator transition into account, a semiconductor point of view is assumed, which covers both the insulating (undoped and doped semiconductor) and the metallic side (degenerate semiconductor) of the transition. The principles of this SHS (S: superconductor, H: semiconductor, German: Halbleiter) approach are explained in chapter 2 alongside the basics of the Josephson effect and the consequences of a semiconducting barrier. In chapter 3 the sample preparation and thin-film analysis results obtained from Nb_xSi_{1-x} films are reported, whereas in chapter 4 an overview of the set-ups used for electrical measurements is given. The main results are presented and discussed in chapter 5. Chapter 6 summarises the results and provides an outlook.

2 Fundamental Considerations

In this chapter the basic theoretic principles required for the present work are described. This includes descriptions of the barrier material used for the Josephson junctions, amorphous silicon, metal-semiconductor contacts and the Josephson effect and its application for voltage standards. The superconductivity part of this chapter is based on the books of Buckel [22], Tinkham [23] and Barone [24], whereas the part about semiconductor properties was compiled with the help of the books of Hunklinger [25], Morigaki [26] and Sze [27].

2.1 NbSi alloys

The first studies of the Nb_xSi_{1-x} system date back to 1941 [28]. A detailed review of the thermodynamic and structural research data acquired between 1941 and 1993 was compiled by Schlesinger and co-workers [29]. Electrical measurements of co-sputtered Nb_xSi_{1-x} performed at the Bell Laboratories revealed a **m**etal-**i**nsulator **t**ransition (MIT) at x≈11.5% and a transition into the superconducting state at x≈18% with a critical temperature of about 10 mK [19][30]. Later studies by a French group on co-evaporated Nb_xSi_{1-x} showed that the MIT occurs at x≈9% while x≈13% was found to be the lowest niobium content with a superconducting transition [20]. Furthermore it was demonstrated that the critical temperature strongly depends on the film thickness [31][32]. Another study on co-sputtered Nb_xSi_{1-x}, which focused on the MIT, obtained a niobium content of about 9.5% for this transition [33][34][35]. This range of results suggests that the MIT is very sensitive to the applied sample preparation method.
From the onset of superconductivity on the metallic side of the MIT the critical temperature rises with the niobium content until x≈75%, which is an extensively studied composition. It has been hoped that Nb_3Si shows a similarly high critical temperature like Nb_3Sn (18.0 K) or Nb_3Ge (23.2 K) [36]. The theoretically predicted value of 25 K [37][38] was never reached, instead it was shown that the critical temperature strongly depends on crystal structure and sample preparation method. Values between 3.4 K and 18 K were reported. This is mainly caused by the coexistence of several crystal structures around x≈75% with each of them exhibiting another critical temperature [29]. Moreover, none of these crystalline phases is stable at room temperature

which prevents the application of Nb_3Si as a superconducting material with enhanced critical temperature.

Figure 2.1 shows the phase diagram of the Nb_xSi_{1-x} system [39]. The crystalline phases are Nb_3Si, α-Nb_5Si_3, β-Nb_5Si_3, $NbSi_2$, Nb and Si [29]. It is clearly visible that both the MIT and the onset of superconductivity are not linked to a transition into a stable phase. Although there are a few metastable phases, all other compositions form thermally unstable amorphous alloys. From previous results on **J**osephson **j**unctions (JJs) with Nb_xSi_{1-x} barriers it is known that typical values for the niobium content *x* range between 10% and 20% [18][17]. A comparison of these values with figure 2.1 shows that these compositions do not belong to any stable crystalline phase. Furthermore the low niobium content suggests that analysis and discussion of Nb_xSi_{1-x} as a barrier material for JJs should start from the limit case of *x*=0%, i.e. pure silicon. Since the Nb_xSi_{1-x} films of the present work were prepared using room temperature DC magnetron sputtering, all prepared silicon films are amorphous. Therefore the first part of the following considerations focuses on the amorphous phase of silicon.

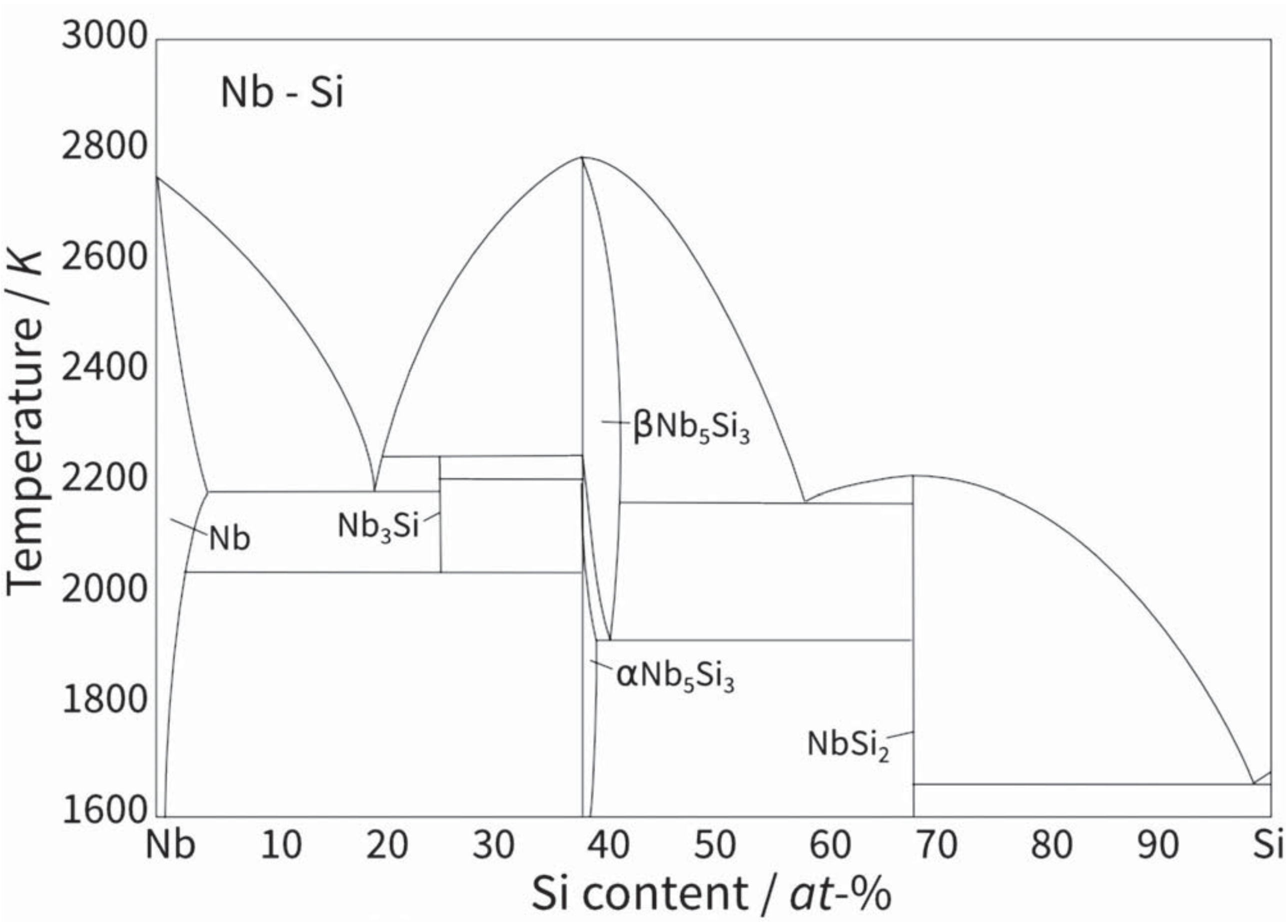

Figure 2.1: Phase diagram of Nb_xSi_{1-x} sketched after [39].