4. TITLE AND SUBTITLE
Sige Quantum Well Infrared Photodetectors (QWIPs) for remote sensing applications

6. AUTHOR(S)
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14. ABSTRACT
This report results from a contract tasking University of Leeds as follows: The contractor will investigate Sige photodetectors. These photodetectors support simpler manufacturing, greater reliability, improved ruggedness and reduced cost when compared with more exotic photodetectors (such as HgTe). The contractor's research will focus on p-type material, which allows for normal incidence absorption of the light and again the possibility of reducing the number of steps in the fabrication, which could lead to greater pixel utilization. The contractor's investigation will also evaluate the potential for increasing the detection wavelength of Sige devices. The mid- and long-wave infrared regions of the spectrum contain many molecular absorption lines; the extension of this to beyond 30 microns will encompass more chemical species and opens up a route for remote gas sensing.

15. SUBJECT TERMS
EOARD, Quantum Dots, IR sensors, Quantum Well Devices
SiGe Quantum Well Infrared Photodetectors (QWIPs) for remote sensing applications:
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This report details the results of a feasibility study into the design and manufacturability of colour (wavelength) sensitive arrays of infrared detectors. The p-type Si$_{1-x}$Ge$_x$ material system was considered because of the potential of absorbing normal incidence light without the need for a surface grating, and because of the future potential of integrating the optical active elements with standard Si electronic circuitry. It is argued that ion implantation could be used to selectively diffuse a lateral arrangement of pixels to tune each pixel to a different peak detection wavelength. In particular a design is given for a quantum well infrared photodetector which detects initially at the lower end of the 8–12 μm atmospheric window, but on diffusing can be made to detect across the entire window. It is suggested that arrays of such devices could be used as a miniature spectrometer for the sensing of atmospheric chemical and biological agents. A comment is made on how they could be deployed in the field and an outline is given for a further project to develop a prototype.
1. In accordance with Defense Federal Acquisition Regulation 252.227-7036, Declaration of Technical Data Conformity (Jan 1997):

"The Contractor, University of Leeds, hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. F61775-01-WE088 is complete, accurate, and complies with all requirements of the contract."

DATE: 11/11/02
Name and Title of Authorized Official: Prof. P. Harrison

2. In accordance with the requirements in Federal Acquisition Regulation 52.227-13, Patent Rights-Acquisition by the U.S. Government (Jun 1989): "Disclosures of all subject inventions as defined in FAR 52.227-13 have been reported in accordance with this clause."

DATE: 11/11/02
Name and Title of Authorized Official: Prof. P. Harrison
1 Introduction

Over the last decade Quantum Well Infrared Photodetectors (QWIPs) have been shown to be an excellent means of detecting mid- and long-wave infrared radiation in the 10-20 microns region of the spectrum. In the previous year Paul Harrison (of The University of Leeds, U.K.) and Richard Soref (of the AFRL Sensors Directorate, Hanscom AFB, MA) have been collaborating on a project, funded by special contract (SPC 01-4007) order number F61775-01-WE007, to translate QWIP designs into the SiGe material system and to push the detection wavelengths beyond current limits. The results indicated that cooling below 77K may not be required for the detection of far-infrared (> 20μm) or Terahertz radiation [1,2].

The SiGe material system is significant because of the possibility of integrating eventual photodetectors with the mass-produced Si-based electronic logic. This would have advantages in terms of simpler manufacturing, leading to greater reliability, ruggedness and reduced cost. In addition, the research has focused on p-type material, which allows for normal incidence absorption of the light and again the possibility of reducing the number of steps in the fabrication, which could lead to greater pixel utilisation. The second point of interest has been the focus of investigating the potential for increasing the detection wavelength of the SiGe devices. The mid- and long-wave infrared regions of the spectrum contain many molecular absorption lines, the extension of this to beyond 30μm will encompass more chemical species and opens up a route for remote gas sensing.

The proposed remote-sensing QWIPs are relevant to AFRL/SN's current efforts to obtain cost-effective, high-performance transceiver sensor systems— including systems operating in the new THz frequency regime and those operating remotely, as from a space platform. SN is seeking efficient, miniaturised solid-state sources and detectors integrated on a transceiver chip. A silicon chip or wafer is an ideal platform for SiGe/Si THz lasers and for the THz detectors described here. The photodetector research of this and the previous contract is therefore relevant to two on-going THz laser projects managed by AFRL/SNHC: Contract F19628-99-C-0074, Vertical Cavity Silicon-Germanium Quantum Cascade Lasers for Terahertz Emission, The University of Leeds, and Contract F19628-00-C-0005, Fabrication of a Silicon-Germanium-Based Quantum Cascade Terahertz Laser, The University of Delaware.

2 Systems for passive remote sensing applications

Sensing systems based on the transmission and detection of electromagnetic radiation have had important military applications since their invention in the middle of the Twentieth century. Radar is the prime example of this technology. It works by transmitting pulses of microwave radiation and detecting reflections from remote objects, such as aircraft and ships, as well as the terrain in navigational aids. While the continuing success of radar is not in doubt, it does have one fundamental flaw—transmission of the initial microwave signal reveals your position. It is now relatively easy to destroy fixed, land-based enemy radar installations by sending missiles which follow the transmitted beam right down into the antenna.

Perhaps, more importantly movable military targets such as ships and aircraft reveal their position whenever they turn their radar on. The only way to avoid looking like a lighthouse is therefore to move to passive rather than active electromagnetic detection.

The human eye is a passive visible light detector and a covert way of detecting incoming aircraft is merely to scan the sky with some optical aid such as binoculars or a telescope. While with nothing
like the range of radar, 'looking' does not reveal your position.

It is this coverness which passive imaging provides that is the motivation behind the systems/subsystems level investigation into the use of SiGe QWIP's for remote sensing in this project.

3 The application: remote sensing of chemical and biological species

The author has been interested in the mid- (4–20 μm) and far-infrared (> 20 μm) or Terahertz region of the spectrum for sometime now and as mentioned above is involved in several projects to design and fabricate sources and detectors of electromagnetic radiation in these wavelength bands. Although there is still much characterisation work to be done, it is known that many molecular species have spectroscopic absorption lines in the mid- and far-infrared regions of the spectrum. Thus, chemical and biological agents, which are being increasingly talked about as weapons of war and terrorism, could be identified by their infrared or Terahertz signature. For examples of the identification of explosives through Terahertz spectroscopy see the work of Van der Weide in [3], page 117 and [4] page 301. For examples of detection of biological agents (anthrax in envelopes) see the work of X. C. Zhang in [4], page 225 and Physics in Medicine and Biology, Special Issue (August 2002) as well as on the internet at: http://www.rpi.edu/~zhangxc.

In this work consideration has been given to a system which could make use of a SiGe-based photodetector, in particular the compactness and ruggedness mentioned above. An application that became apparent was that of theatre protection from airborne chemical and biological agents. While it is possible that such weapons could be delivered directly into a sensitive area such as an airfield or defensive position via a missile, a more likely route in a theatre of war against a low-tech. aggressor would be simply through release into the atmosphere upwind. In this scenario there would be no warning against the arrival of such species. The way to guard against this type of attack would be to put remote sensing stations at various distances from the area to be protected.

4 System considerations

Perhaps the obvious route to detection of airborne species would be a system as illustrated in Fig. 1. If the source was a laser then detection of chemical species would be through a single absorption line. A more accurate and reliable sensor would require multiple absorption lines, which would either require several laser–detector pairs or a broad band source and a detector with wavelength sensitivity.

Alternatively a QWIP-based staring array is entirely passive and can sample a much greater volume of atmosphere using the background radiation as the source, see Fig. 2. This principle is similar to the absorption lines of the sun’s radiation—the sun generates a continuous spectrum but the atomic species in the sun’s atmosphere absorb light at particular frequencies giving rise to dark bands. In addition, without the infrared source, this system will be much more compact, and therefore more difficult to find and destroy. Furthermore, the reduced power consumption will allow for a longer battery life and sensing lifetime.
5 **Miniature spectrometers**

In some applications the passive detector in Fig. 2 could be a focal plane array *imaging* system. This would require sophisticated image processing software to identify objects such as tanks, ships or airplanes. In the application discussed here it is the recognition of chemical and biological species through their infrared absorption spectra that is of interest. Thus the detector would not be a focal plane array for imaging, it would require frequency (wavelength) sensitivity—it would need to be a colour sensitive array.

Fig. 3 shows a colour sensitive array at the subsystem level. A diffraction grating disperses the incoming radiation according to its wavelength onto a linear array of detector pixels.

Standard QWIP technology can fabricate arrays with $256 \times 256$ elements, thus a linear array of say 256 pixels (each say, 30×30 microns with a 10 micron spacing) is easily achievable. Now the new technology is to make each of the pixels sensitive to a different wavelength of radiation, so that the array can sample a spectrum between say 4 and 8 microns, or 12 to 14 microns with 256 sampling points. This could be achieved by designing a QWIP to work at the shortest end
of the required wavelength band and then selectively diffusing each pixel in turn. This could be achieved by ion implantation which can reach the required focusing accuracy. The ion implantation introduces defects into the lattice which enhance diffusion of the material species. Thus in the Si$_{1-x}$Ge$_x$/Si system, the Ge diffuses out of the well and produces a curved rather than flat profile, at the same time the confinement energy of the holes increases and hence the absorbing wavelength increases, see Fig. 4. This principle of tuning the wavelength of a QWIP using ion-implantation assisted diffusion has already been demonstrated [5].

6 Colour sensitive arrays

Having identified the route to a subsystem, attention can now be turned to realising its heart—the color sensitive array. Naturally semiconductor wafers are grown in large array formats with a laterally uniform structure, see Fig. 5. Thus, arrays of devices produced by traditional photolithography are all based around the same semiconductor layer structure and hence all have the same absorption wavelength.
It is proposed in this work to consider the possibility of patterning the substrate before the photolithographic stages, in order to change the absorption wavelengths of the semiconductor layer structure at different points across the wafer. This could be achieved through 'direct writing', possibly with the use of a mask. There are two possible approaches that could be used:

1. Laser induced annealling [6]

2. Ion-implantation induced diffusion [7, 8]

Both of these techniques create a diffusion of the material species from the quantum well into the barrier and vice versa, hence it is often referred to as 'inter-mixing' of the heterojunction. In the laser induced annealling, a laser is focussed onto an area of the semiconductor wafer and the wavelength and intensity of the light are chosen such that the absorption of the photons produces sufficient local heating to allow the atomic species within the crystal lattice to move. The thermal energy input into the crystal does disperse over time and hence there will be some limit to the controllability (blurred edges). The second technique, ion-implantation, fires a beam of inert ions (charged atoms) at the surface, which then penetrate the crystal and collide with the atoms in the lattice, which can knock atoms out of position thus producing vacancies. The vacancies provide sites for other atoms to move into and a mixing of the atoms can occur. The depth to which the ions penetrate depends on the energy of the impinging ions (the higher the energy the deeper the penetration) and hence there is some control over the depth of the mixing.

Both of these processes lead to a diffusion of the atomic species within the crystal which can give the potential to pattern the substrate laterally. In order to be able to design devices based on either of these principles it is necessary to be able to model the diffusion and its consequences. These two points will be addressed in the following sections.

7 Diffusion modelling

In order to be able to deduce the possible band width of a colour sensitive array formed by diffusion it is necessary to be able to model the diffusion process. Fick's second law of diffusion (in one-dimension $z$) gives:

$$ \frac{\partial x}{\partial t} = \frac{\partial}{\partial z} \mathcal{D} \frac{\partial x}{\partial z} $$

(1)

where $x$ is the concentration of the diffusant at any time $t$ and any point $z$ along a one-dimensional axis and $\mathcal{D}$ is the diffusion coefficient, which can be a function of $x, z,$ or $t$. 

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The author has introduced a numerical solution of equation (1) which iterates forward in time the distribution of the diffusant $x$ as a function of $t$. In particular:

$$x(z,t+\delta t) - x(z,t) = \frac{D(x,z+\delta z,t) - D(x,z-\delta z,t)}{2\delta z} \times \frac{x(z+\delta z,t) - x(z-\delta z,t)}{2\delta z}$$

$$+ D(x,z,t) \left[ \frac{x(z+\delta z,t) - 2x(z,t) + x(z-\delta z,t)}{(\delta z)^2} \right]$$

Given that the original ($t=0$) profile of the diffusant $x(z,0)$, is known, then equation (2) can be iterated forward for any given mathematical form of $D$ to predict the profile some time later, i.e. $x(z,t)$.

![Graph showing Ge concentration as a function of depth after various diffusion times.](image)

Figure 7: The Ge concentration as a function of depth $z$ after various diffusing times.

This mathematical/computational model allows the functional form of the diffusion coefficient to remain completely general. In the list below some examples of the form of $D$ are discussed:

1. $D = D_0$, a constant, for simple diffusion problems.
2. $D = D(x)$, a function of the concentration as encountered in non-linear diffusion problems [9]. Note, that as $x = x(z)$ then $D$ is intrinsically a function of position too.

3. $D = D(z)$, a function of position only, as could occur in ion implantation problems [10]. Here the diffusion coefficient could be linearly dependent on the concentration of vacancies for example, where the latter itself is depth dependent.

4. $D = D(t)$, a function of time, as could occur during the annealing of radiation damage. For example, ion implantation can produce vacancies which aid diffusion [11, 12]. During an anneal, the vacancy concentration decreases as the lattice is repaired, which in turn alters the diffusion coefficient.

The solutions are constrained under the boundary conditions that the concentration of the diffusant at either end of the system is the same as that calculated for the adjacent point—physical this means a closed system with the total amount of diffusant remaining constant, see Harrison [13].

Fig. 7 gives an example of this numerical solution to the diffusion equation. It shows the results of calculations of the effect of diffusion on a 40 Å wide Si$_{0.8}$Ge$_{0.2}$ quantum well surrounded by Si barriers, for a constant diffusion coefficient $D$ of 1 Å$^2$s$^{-1}$. As expected the Ge diffuses out of the well, which would lead to an increase of the potential of the bottom of the well, reducing the ionisation energy of confined carriers. Thus the detection wavelength of any QWIP subject to diffusion would be increased, so it seems that this might be a promising route to achieve the goal of a colour sensitive array.

8 The electronic structure of Si$_{1-x}$Ge$_x$ quantum wells

![Figure 8: The hole energy levels as a function of the quantum well width for (a) Si$_{0.8}$Ge$_{0.2}$ and (b) Si$_{0.7}$Ge$_{0.3}$ quantum wells surrounded by Si barriers.](image)

It is now necessary to focus on a particular material system, and a particular QWIP design in order to evaluate the potential of this approach. With this aim calculations of the hole energy levels
in single $\text{Si}_{1-x}\text{Ge}_x$ quantum wells were performed for a variety of different Ge concentrations $x$. Fig. 8 shows the results of some of these calculations.

Fig. 8 plots the hole energies as a function of the width of the quantum well for (a) $x = 0.2$ and (b) $x = 0.3$. The nature of the hole subband within the quantum well is labelled, for example HH implies heavy-hole, LH light-hole and SO implies that the state has a character derived from the split-off band. The calculations were performed using a commercially available 8-band k.p calculation\(^1\). The semiconductor heterostructure was taken as a free standing, which implies that it is strain-balanced to a $\text{Si}_{1-x}\text{Ge}_x$ buffer, where the alloy concentration $y$ is chosen so that the lattice constant of the buffer is equal to the average lattice constant of the quantum well stack.

The dashed vertical arrows on Fig. 8 show possible configurations for normal incidence bound-to-quasi-bound quantum well infrared photodetectors. The ground state in this material system is always a heavy-hole (HH) level, thus the normal incidence criteria is satisfied by having an absorption transition to a subband of a different character, in this case either LH or SO. The bound-to-quasi-bound criteria is satisfied at well widths where an excited hole level is located near the top of the barrier potential (given by the horizontal dashed lines).

The transition energy between the HH and LH/SO2 subbands in Fig. 8(a) is 0.111 eV which equates to 11.2 $\mu$m. In part (b) the corresponding transition energy is 0.157 eV which corresponds to 7.9 $\mu$m. Considering the 8-12 $\mu$m atmospheric windows as the range of wavelengths of interest, then the initial 'as grown' quantum wells must be designed to absorb at the shortest wavelength (highest energy), i.e. 8 $\mu$m. This is because the diffusion process, no matter how it is induced, leads to intermixing and a reduction in the confinement energy of the holes. This is always the case whether a $n$-type systems is used, or whether the alloy material constitutes the barrier as opposed to the quantum well.

The target wavelength of 8 $\mu$m is between the two structures illustrated in Figs. 8(a) and (b) and is much closer to (b). This was used as a starting point for the design, and after further calculations, a bound-to-quasi-bound structure was found which would absorb at 8 $\mu$m. The alloy concentration in the well was found to be 0.28 and the width of the quantum well was 34 Å.

9 Using diffusion for post-growth tuning of the detection wavelength

In a real situation laser induced or ion implantation enhanced diffusion will lead to a depth dependent diffusion coefficient. This can be simulated via the numerical model above [13], however for the purpose of illustration here, a constant diffusion coefficient will be taken i.e. $D = D_0$, and in this case was given the numerical value of 1 Å\(^2\) s\(^{-1}\).

Fig. 9 shows the results of diffusion simulations using this constant diffusion coefficient for the 34 Å $\text{Si}_{0.72}\text{Ge}_{0.28}$ quantum well surrounded by Si barriers, which has been chosen (as discussed above) to absorb at 8 $\mu$m. It can be seen from the figure that the initial $t = 0$ rectangular distribution of Ge which produces the quantum well, diffuses out of the well (at the same time Si from the barrier diffuses into the well) smoothing the profile. Note that, as the total amount of Ge in any one period remains constant, then the quantum well stack will remain strain-balanced throughout the diffusion process.

\(^1\)Available from Quantum Semiconductor Algorithms, see http://users.riken.com/qsa/Index.html
Figure 9: The Ge concentration $x$ for the 34 Å Si$_{0.72}$Ge$_{0.28}$ quantum well surrounded by Si barriers, after various diffusion times.

As the time of diffusion increases the peak in Ge concentration decreases from the initial value of 0.28 and reaches just 0.20 by $t = 120s$. This decreasing Ge concentration reduces the depth of the quantum well and hence the intersubband absorption transition energies will also decrease.

With this constant diffusion coefficient ($D = D_0$) the diffusion profiles are universal in the product $D_0t$. Thus if the diffusion coefficient was measured to be 2 Å$^2$s$^{-1}$, rather than the 1 Å$^2$s$^{-1}$ employed in the simulations here, then the results can be translated.

Figure 10: The Ge concentration $x$ for the 34 Å Si$_{0.72}$Ge$_{0.28}$ quantum well surrounded by Si barriers, *discretised* at each monolayer for diffusion times of $t = 10$ s and $t = 100$ s.

The diffusion simulations require a relatively small step length $\delta z$ (see equation 2) in order to achieve numerical stable results and convergence. The value of this parameter is usually in the range
0.1–1.0 Å which is much smaller than the lattice constant of the Si_{1-x}Ge_{x} quantum well stack. The latter varies between 5.43 Å for pure Si and 5.66 Å for pure Ge. Now the k.p program requires the semiconductor heterostructure to be input as a series of layers, so it is necessary to discretise the continuous diffusion profile as in Fig. 9 to a series of layers of integer multiples of monolayers in thicknesses. This results in potential profiles as plotted in Fig. 10. Note the absorption wavelength is calculated from the resulting confined heavy-hole level to the band edge.

10 Spanning the 8–12 μm atmospheric window

![Detection wavelength as a function of diffusion time](image)

Figure 11: The detection wavelength λ as a function of the diffusion time t for the (originally) 34 Å Si_{0.72}Ge_{0.28} quantum well surrounded by Si barriers.

Fig. 11 shows the results of the calculations of the absorption wavelength as a function of the diffusion time. It can be seen from the figure that the quantum well was initially (t = 0) designed to absorb at 8 μm and as the Ge is allowed to diffuse the full range of wavelengths up to 12 μm can be obtained. Thus, referring back to Fig. 3, the procedure to fabricate a colour sensitive array is, to leave the first pixel as it was grown, and then diffuse each pixel in turn along a line to a greater degree until the last pixel is diffused to the equivalent of D_0 t = 1 Å²s⁻¹ × 120 s = 120Å², which would tune it to absorb at 12 μm.

One point to note is, that the wave function shape changes slightly as the quantum well profile diffuses, which affects the intersubband optical matrix element slightly. This could be accounted for by calibration of the response of each individual pixel, which would be a one-time procedure for each different type of array.

11 Deployment

Components and fabrication techniques have been proposed which could be constructed into a subsystem for use as a miniature spectrometer for chemical sensing. It is likely that the first subsystem
proposed in Section 4 could be as small as a book, with the latter system, the staring array, being as small as a mobile cellular phone. Such compactness gives the devices another advantage—they are exceedingly easy to hide and one could envisage creating a ‘perimeter fence’ of detectors by parachute drop from an aircraft, see Fig. 12.

![Diagram](image)

Figure 12: Operational deployment.

Even in a bare desert environment, the devices would be so small that they would give only the profile of a rock and would be virtually undetectable. They could communicate to an airborne listening station through an RF link, which in turn could be directionised to reduce the chances of detection.

12 Summary

- **System ideas**: A miniature spectrometer as a device for remote sensing applications was conceived. A colour sensitive array has been identified as the route to obtaining sufficient spectral resolution in the mid- and far-infrared wavelengths.

- **Viability of fabrication procedure**: Literature studies and discussions with other workers have established ion implantation as a catalyst for diffusion and the possibility of selective ion implantation across areas of several square mm with resolutions of a few microns.

- **Diffusion modelling**: A numerical simulation of diffusion has been applied to the Si$_{1-x}$Ge$_x$/Si system.

- **Design of diffused quantum wells for 8–12 μm detection**: It has been shown that a Si$_{1-x}$Ge$_x$ quantum well can be designed to absorb infrared light of 8 μm wavelength, and that diffusion of this quantum well could lead to absorption across the entire 8–12 μm atmospheric window.
13 Suggestions for future projects for the realisation of the colour sensitive infrared arrays

This project has been a feasibility study to see if such devices could even be designed, whether it was feasible enough to have a quantum well infrared photodetector and to tune its wavelength significantly through diffusion and the altering of the well shape. That has been achieved.

If the work was to continue then funding could be supplied at two different levels:

1. **Further theoretical design work:** There is room for more design work. The diffusion modelling has used a 'global' diffusion coefficient to describe the intermixing of the Si-Ge interface on average. This could be done more accurately and a more realistic description of the diffusion process could also be included. The latter would involve the inclusion of a T.R.I.M. code simulation of the lattice damage (the vacancy distribution) in the quantum well stack. This would allow the ionic species and the implantation energy and dose to be optimised for our purpose. The depth dependence of the diffusion coefficient could then be included in the simulations and indeed the final annealing process to repair the lattice damage. Knowledge of the depth dependence of the diffusion coefficient would also give information on the inhomogeneous broadening of the absorption spectrum.

Calculations of the intersubband optical matrix elements as a function of the diffusion time would allow the sensitivity of each pixel to be evaluated, thus allowing the arrays to be calibrated from theory.

Other central frequencies could be considered. For example, the 3–5 \( \mu \text{m} \) atmospheric window is particularly interesting as many hydrocarbons have absorption lines in this region. Thus the potential of the technology for environmental sensing could be demonstrated.

Such work could probably be performed under the same special contract scheme that has funded this project.

2. **Development of a prototype device:** The experimental realisation of a colour sensitive array in this material is the ultimate technology demonstrator.

Some steps are already being made in this direction by the author (Paul Harrison) via two other projects. The first project has already been funded by the EPSRC (U.K.) under their 'Basic Technology Initiative'. Funds have been secured to obtain GaAs/GaAlAs quantum well samples and to have them ion implanted at the EPSRC central facility at the University of Surrey. Discussions between Paul Harrison and Dr. Chris Jeynes at Surrey have confirmed that direct writing via an ion beam on the scale of pixels (lateral extent of the order of 10 \( \mu \text{m} \) or so) and over areas of a few \( \text{mm}^2 \) is feasible. The aim is to develop colour sensitive arrays in GaAs for the long wavelength infrared.

The second project is a collaboration between the author and colleagues UMIST and the University of Southampton. In this project, which is still at the proposal stage, we intend to develop the growth technology for the fabrication of Si\(_{1-x}\)Ge\(_x\) quantum well (and dot) infrared photodetectors. The proposed project also includes funds for spectroscopic characterisation, electro-optic measurements and theory and design.

This same collaboration could be employed to marry the technology of the direct-write ion implantation to the SiGe QWIPs to produce prototype devices as described in this report. This would, however, require more substantial funding.
References


