NSLS-II Beamline Development Proposal

Type I [X] Type II [ ]

Materials Physics and Processing Beamline (MPP)

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Summary

This is a proposal for the development of a beamline that will be optimized for 1) real-time, *in-situ* studies of phase transformations of thin blanket films, stacks, and nanopatterned samples, and 2) x-ray diffraction and scattering techniques on solids, including thin films, stacks, nanopatterned samples, and bulk materials, with the capability for mounting small environmental chambers, bending jigs, and Displexes.

The science programs to be addressed are these: 1) microelectronics materials research (both real-time, *in-situ* characterization during thermal annealing and XRD measurements of texture, strain, ripening, diffusion, roughening and phase identification), 2) real-time nanocatalyst phase transformations, and 3) solid state physics (primarily resonant scattering of 3d and 5d complex materials and scattering in a magnetic field). The beamline will utilize a 3-pole wiggler source and a double-crystal monochromator designed for rapid switching between multilayer and Si(111) crystal sets to provide choice of high-flux or high-resolution beam to two endstations in tandem: 1) a robotically controlled real-time, *in-situ* endstation for high-throughput rapid thermal annealing (RTA) and isothermal measurements, and 2) a 6-circle diffractometer with capability for mounting small sample environmental chambers and processing stages. Remote access, automated running on the RTA endstation, and rapid switching of beam between the endstations will permit rapid access and high throughput of experiments. IBM is interested in discussing a collaboration with NSLS-II regarding the upgrade of our unique *in-situ* RTA capability to become a high-throughput, robotically-controlled operation with remote access.

Background

The science programs to be supported by this beamline have had a long and productive history at the NSLS. Solid state physics, materials science, and semiconductor research use many of the same x-ray techniques, analyses, and theory. The proposal team has performed their research primarily among the X20, 21 and 22 beamlines.

IBM has been involved at the NSLS since its beginning, and in collaboration with Robert Birgeneau (then at MIT) built beamlines at port X20 in 1984-5 for solid state physics and microelectronics materials research. The beamlines were a model for academic/industrial partnership under the PRT system until IBM became sole proprietor in 2002. They have produced over 350 publications and 70 student theses over 26 years. The list of student names (see Appendix 4) includes some of today's prominent synchrotron scientists. The main techniques used are 1) millisecond-resolution *in-situ* XRD, resistance and light-scattering measurements during rapid thermal annealing (RTA) of thin films and nanostructures, 2) texture measurements (pole figures) of thin films and nanostructures, and 3) standard diffraction techniques for materials characterization, such as HRXRD, GIXD, and XRR. These techniques are of great importance as tools for understanding the materials, developing the processes, and solving the manufacturing problems related to successful evolution of microelectronics technology.

Beamline X21 is a facility beamline owned and operated by the NSLS. In 2004 it was upgraded and a programmatic change from inelastic to elastic x-ray scattering was made. X21 is now the only NSLS insertion device beamline dedicated to solid state physics and materials science studies, and since 2009 has had three research programs: 1) scattering in a high (13 T) magnetic field, 2) high-resolution scattering, and 3) real-time materials growth and processing.

Condensed matter research has a long history at the X22 beamlines. X22C was built in the mid-1980's by the X-ray Scattering Group, now of BNL's Condensed Matter Physics and Materials Science Department, and is operated by them to this day. The programmatic focus is on resonant and non-resonant x-ray scattering studies of electronic order at surfaces and in the bulk of novel electronic materials, particularly transition metal oxides. It has a long and productive history including many seminal results in the field of resonant scattering and surface scattering. Approximately 30 publications were produced in the period 2005-2009.

Building on our experience as beamline and endstation designers, builders, operators, and users, with important science programs currently at the NSLS, we want to seize this opportunity to combine our expertise and guide the creation of a beamline at NSLS-II where our programs and instrumentation can continue to flourish. It also will provide core capabilities for our communities' research programs. In addition, IBM and collaborators are eager to upgrade our unique *in-situ* RTA capability to become a high-throughput, robotically-controlled operation with remote access.

A. Science Case

The scientific case for the MPP beamline involves the evolution of current NSLS programs in solid-state physics, materials characterization and real-time processing. The development of high-throughput, remote access with fast switching between two endstations will result in efficient use of resources, increased convenience, and growth of industrial usage. Sections A1-A3 describe three distinct scientific programs: microelectronics research, measurements during real-time materials processing, and solid state physics. Sections A4 – A6 describe other significant aspects of the science case.

A.1. Microelectronics Industrial Research

The MPP beamline will be optimized for ultra-thin film and nanostructure analysis by researchers in the microelectronics industry, universities, and government laboratories. These ultra-thin films and nanostructures, such as high-k dielectrics for transistor gate oxides, diffusion barriers for lining the trenches and vias of copper interconnects, and layered magnetic materials for Magnetic Random Access Memory, are critical components of future generations of microelectronics devices. High-precision, non-destructive structural characterization, including phase identification, texture, grain size, and strain analysis, is essential in the development of these materials and the understanding of their performance. In addition, we use synchrotron x-rays to measure phase transformations and other processing effects, *in-situ*, during rapid thermal annealing. Our research ranges from understanding basic properties and behavior of materials, through development of new materials and processes for specific technologies, to troubleshooting problems that appear during chip fabrication. Materials, processing, and metrology will continue to evolve to meet the demands laid out by the International Technology Roadmap for Semiconductors (ITRS)[1]. We have very fruitful collaborations with academic institutions and other microelectronics companies, along an "R&D continuum" which is summarized in the figure below.

Figure 1.

The following subsections highlight important microelectronics technology issues for the near and distant future that the MPP beamline will help to address.

A.1.a. Real-time, in-situ characterization of microelectronics materials during rapid thermal annealing *(C. Lavoie, S. Raoux and J.L. Jordan-Sweet, IBM)*

IBM has developed a unique synchrotron capability through the design, building, and operation of a specialized diffraction endstation in which time-resolved measurements of characteristic diffraction peaks from changing materials are performed *in situ* during Rapid-Thermal-Annealing (RTA). (RTA is a common step in many parts of the chip manufacturing process.) Two other probes, operated simultaneously with XRD, are a four-point probe to measure thin film resistivity, and optical light scattering to measure surface morphology changes on the 0.5- 5 μm lengthscale. The use of this endstation at X20C has produced numerous publications, contributed to many student theses, and has led to important innovations in semiconductor materials and process development**.** Rapid characterization of over one thousand samples per year permits us to evaluate large matrices of process conditions and starting materials, and the quick feedback of results allows us to pursue promising directions and eliminate unproductive avenues with great efficiency. The most significant outcome has been the continued improvement of metal silicide contacts to the device level in CMOS Field Effect transistors (FETs) and memory[2]. This program has impacted three generations of metal silicides: $TiSi_2$ (250nm technology node)- demonstrating improvement in nucleation of C54 $TiSi_2$ in small contact areas by using Nb or Ta alloys to increase nucleation density[3]; $CoSi_2$ (180–90nm nodes)- improving interface smoothness through alloying[4], and NiSi (90nm–future nodes)- addition of Pt to extend film stability to higher temperatures[5].

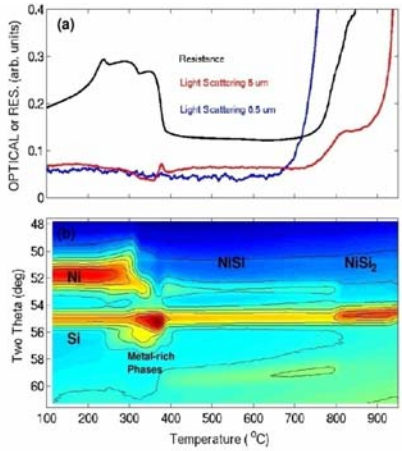
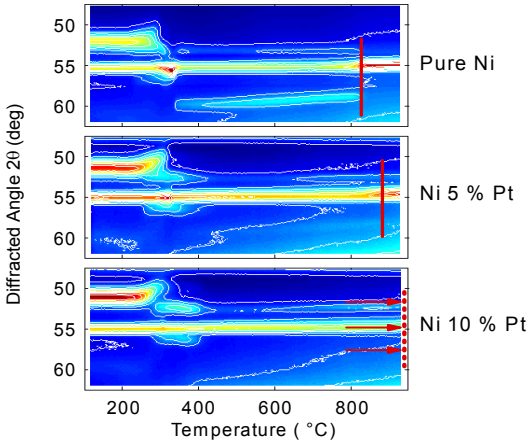


Figure 2

(a) Resistance and light scattering from 0.5 and 5 mm length scales and (b) diffracted x-ray intensity contours over an angular spread of 10 degrees in 2θ, measured by a linear diode array detector as a function of sample temperature. The samples were ramped from 100 to 950C at 3C/sec.
(c) Series of RTA plots showing effect of Pt alloying on increasing thermal processing window for low-resistance NiSi phase.



Another important technology that has relied on this technique for materials development is "universal" memory based on phase change materials. Many studies have been performed using *in-situ* RTA to measure crystallization temperatures for candidate chalcogenide materials[6]. In addition, scaling effects of decreasing film thickness (down to 2nm) and nanostructure size are being studied[7].

Other chip component research that benefits from this technique includes diffusion barrier failure[8], formation of lead-free solder bonds[9], and formation of ohmic contacts to carbon-based device materials[10]. Kinetics studies also can be performed on all of these processes by measuring the phase transformation temperature either as a function of annealing ramp rate or as a function of isothermal hold temperature.

It is extremely important for us to have access to this unique synchrotron tool, and to develop an improved thermal processing endstation to expand on the capabilities that will be lost at NSLS beamline X20C when it is shut down. Improvements to this *in-situ* system will allow for remote running and high throughput, as well as adding XRR, SAXS, and texture evolution capability to XRD, resistivity and light scattering. This automated endstation will enable efficient and convenient use of resources and expand the industrial user base.

A.1.b. Texture *(C. Detavernier, Ghent U and J.L. Jordan-Sweet, IBM)*

In micro-electronics, metal-Si compounds are used to contact the active regions of the transistor. These silicide layers are usually formed by a solid-state reaction between a deposited metal film and the Si substrate. The continued decrease in line width makes it increasingly important to characterize and control the microstructure of the contact layer. In some cases silicide lines are, in fact, bamboo structures of a single row of grains. The orientation, or texture, of these grains determines their interface structure and energy, and therefore influences important properties such as work function, barrier height, contact resistance, agglomeration resistance and phase formation sequence.

In recent years, we have made a detailed study of the texture of various silicide phases. For NiSi layers, we observed complex patterns on the pole figures which could not be explained on the basis of the existing classification of texture in thin films. Further research showed that several silicide phases (NiSi, $CoSi_2$, alpha-$FeSi_2$) exhibit a new type of texture, which we called 'axiotaxy'[11]. Axiotaxy (1D periodic interface) can be considered as an intermediate case between epitaxy (2D periodicity) and a random interface (no periodicity).

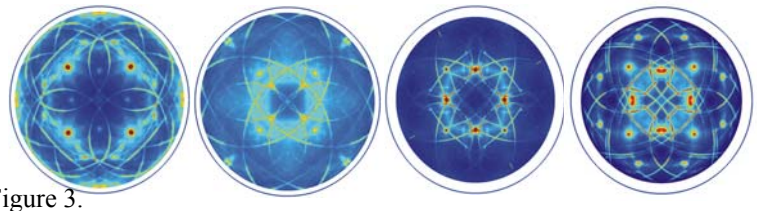


Figure 3.
Pole figures showing axiotaxy for NiSi/Si(001): (202)/(211), (002), (103), and (112).

This type of texture has ramifications for the performance and failure of CMOS devices. By adding a few at% of a different metal to the Ni, the axiotaxy can be eliminated and the thermal budget for processing without causing silicide/Si agglomeration can be increased[12]. This technique also is being used to determine the effects of scaling on texture by measuring arrays of nanoscale silicide features which model the actual contact area. The use of a linear avalanche diode array strip detector developed at the NSLS has streamlined our measurements, enabling us to take 640 simultaneous pole figures in a period of several hours.

In the future, this ongoing research on thin film texture will be extended towards other materials (e.g. germanides as contacts for Ge or III/V semiconductors). Secondly, further scaling will demand a continued reduction in the thickness of the contacting layer. Because of the reduced thickness, interface effects will become increasingly important, and metastable phases may become relevant. Studying phase formation and texture in these ultra-thin contacts (thickness < 5nm) will require a high flux and 1D or 2D detectors with a large dynamic range.

A.1.c. Strain *(C.E. Murray, IBM Research)*

During manufacture, metallization used in microelectronic circuitry experiences significant changes in its stress state due to numerous thermal excursions resulting from subsequent processing. The difference in coefficient of thermal expansion (CTE) between Cu, the current choice for metallization due to its high conductivity, and its environment often drives the metallization features into compression during heating and tension after cooling to room temperature. The creation of voids, which can occur due to residual stress in the Cu metallization, represents an important reliability issue, particularly as device dimensions decrease and power densities increase. Since the interface between the Cu metallization and capping layers represents a location that is susceptible to electromigration-induced mass flow, it is critical that the evolution in stress in this region be understood. *In-situ* investigations of these buried interfaces, through the use of conventional x-ray stress measurements and glancing incident X-ray diffraction can provide crucial learning with respect to conductor longevity and reliability[13].

A.1.d. Real time, in-situ quantification of self-annealing*: (Cev Noyan, Columbia U)*

In the past decade, there have been numerous investigations of the room temperature self-annealing phenomenon found in electroplated copper thin films. The as-plated polycrystalline films typically have grain sizes in the 50-200 nm range, and grow through the thickness of the film with lateral dimensions on the order of microns. In addition, the self-annealing process is anomalous, with only certain grains growing in a matrix of small grains until the small grains are consumed. To characterize grain size and growth kinetics, direct methods such as plan-view focused-ion-beam (FIB) imaging and cross-sectional transmission electron microscopy (TEM) have typically been employed. Determination of growth kinetics with these techniques is complicated and tedious: in FIB imaging, the implantation of ions causes pinning of the grain boundaries and subsequent images require scanning of different regions; TEM based techniques require significant sample preparation and require multiple samples due to the destructive nature of replica preparation. Indirect techniques, such as electrical resistivity measurements, present calibration difficulties.

Time-resolved measurement of x-ray diffraction peaks offers a direct method to quantify film texture, grain size, grain perfection and lattice strain, in controlled atmospheres and as a function of temperature, with virtually zero sample preparation. Our initial measurements on Cu films have yielded significant new information on the recrystallization behavior of various texture components and the concomitant variation of lattice strain. These measurements are gated by the incident x-ray beam size and intensity. The availability of

high intensity, small spot x-ray beamlines will enable characterization of the transformation characteristics of smaller volumes and enable the analysis of recrystallization heterogeneity in real time.

A.1.e. Microelectronics materials characterization *(J.L. Jordan-Sweet, IBM)*

Another important industrial use of synchrotron x-rays is for "standard" types of materials characterization in cases where the capabilities of in-house diffraction tools are inadequate. The advantages can be in flux, brightness (small beam-size) and/or energy tunability. Properties such as crystalline phase, film layer thickness and density, interfacial roughness, grain size, epitaxial orientation, and texture can be characterized. Recent applications of these techniques include: 1) phase identification of ALD- and CVD-grown $La_xLu_{x-1}O_3$ ultra-thin (2nm) high-k dielectrics[14], which are used to replace SiO_2 as the gate insulator in CMOS FETs; 2) grain size measurements on Phase Change Materials in a study relating glass transition temperature prediction, crystallization temperature and speed, and grain size for a series of metal-doped GeSbTe thin film samples[15]; 3) roughness of CoSi/Si interface and top surface to determine the effect of alloying on contact film quality, resulting in US patent #6809030; and 4) temperature-dependent XRR to measure the density and roughness of HfO_2 thin films[16].

A.2.: Real-time evolution of solid state materials systems

A.2.a. Phase transformations in metallic nanocatalysts *(O. Malis, Purdue U)*

Synchrotron-based, real-time x-ray diffraction is being used to study the phase and morphological transformations in a class of nanomaterials of interest to energy-related applications: multi-metallic nanoparticles. Nanomaterials exhibit structural properties that often sharply contrast with the properties of their corresponding bulk counterparts. The high-flux of the synchrotron x-ray source is not only convenient because it drastically reduces characterization time, but absolutely necessary to examine the fine structural details of the small volumes of nanomaterials. Moreover, the synchrotron x-ray source offers unparalleled capabilities to unravel the early stages of the transformations by following the processes in real time with sub-second resolution. So far we have been focusing on the structural evolution of Pt-based nanoparticle catalysts synthesized from solution. These nanomaterials are believed to represent a viable pathway towards improving the performance of fuel-cell catalysts. Using *in situ*, real-time, synchrotron-based XRD, we have been exploring nanoscale size effects on the kinetics of processes such as growth, melting, alloying, ordering, and phase segregation in Pt-Au nanoparticles. These experiments were only made possible by the compact rapid-thermal annealing chamber available on beamline X20C at the NSLS. A highlight of our studies is the observation of melting and re-solidification of Au-Pt alloyed nanoparticles at temperatures below 200°C.

The proposed MPP beamline is essential for insuring the continuity of these types of material studies in the future. There are numerous other multi-metallic nano-material systems (PtVFe, PtNiFe, PtNiCo, PtNiZr, PtNiTi, etc.) that would benefit from the enhanced brightness and reduced beam-size of the x-ray source at NSLS-II combined with the in situ processing capability. Since the transformations are typically irreversible, the planned robot sample change would allow for rapid and/or remote sample change, therefore enabling more efficient mapping of the vast parameter space (i.e. temperature, composition, particle density, particle size) of nano-scale phase transformations. We are also interested in performing in situ real-time XRD studies of AuPt nanoparticle phase and size evolution during accelerated electrochemical stability tests. For this purpose a small environmental (electrochemical) cell will be designed and mounted on the 6-circle diffractometer in the second endstation of the MPP beamline. The goal is to search for evidence of particle coarsening, shrinking, coalescence or dissolution due to electrochemical cycling in order to ultimately clarify the processes responsible for nano-catalyst instability during electrochemical operation.

A.3: Solid State Physics: *(C. Nelson, BNL and V. Kiryukhin, Rutgers U)*

The proposed beamline will allow studies of materials on the forefront of condensed matter science. Because of significant resonant enhancement, magnetic signals, multipolar orders, the effects of spin-orbit coupling, and the effects of crystal environment could be studied throughout the lanthanides and through most of the 5d elements (L edges). In 3d elements (K edges), effects of charge and orbital order, as well as of nonspherical charge distribution could be investigated. The beamline will be optimized to utilize the major unique advantages of the RXS technique, such as element specificity, spin/orbit selectivity, sensitivity to multipolar order, orbital phase sensitivity, and— due to its high brightness— the ability to investigate

microscopic samples. The beamline will provide a versatile facility for a broad range of cutting-edge projects, both in fundamental science, and in applied research.

Interest in 5d materials has exploded recently with discoveries of novel states of matter, such as topological insulators[18] and quantum spin Hall materials[19]. The uniqueness of the 5d systems lies in the interplay of equally strong spin-orbit interaction and electronic correlations. It leads to unconventional electronic states that cannot be described using the language of weakly-interacting spin and orbital states. Resonant x-ray scattering (RXS) is a unique tool to probe these states. In Sr_2IrO_4, for example, quantum interference properties of the RXS were used to reveal the complex $J_{eff} = 1/2$ state of the Ir ion (Fig. 4)[17], and

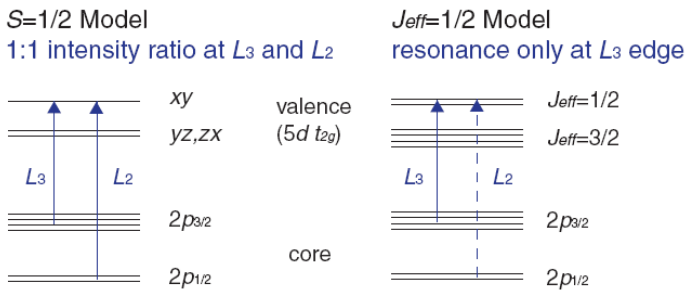


Figure 4. Electronic transitions responsible for the resonant enhancement of the magnetic reflections at the L edge in Sr_2IrO_4.[17] Analysis of the experimental data allows to distinguish between the S=1/2 model applicable to lower-z elements, and the J_{eff}=1/2 model taking into account relativistic effects and applicable to the 5d elements.

thus a novel spin-orbital Mott state has been discovered. This state has been proposed to give origin to a novel topological state of matter and quantum Hall effect in hexagonal lattices, and is relevant for quantum computing[20]. A large number of other intriguing 5d compounds are awaiting investigation. Ir systems, in particular, exhibit anomalous magnetic states ($Sr_3Ir_2O_7$)[21], spin-Hall effect (Na_2IrO_3), and unconventional dimerized orbital states ($CuIr_2S_4$)[22,23]. RXS can provide definitive insight into the nature of their electronic states. High spin-orbit coupling characteristic to the 5d materials is important for many other fundamental and applied topics in solid-state science. Multiferroic materials[24], for example, require large values of this coupling for enhancement of magnetoelectric effects, and search of 5d-based systems (based on Ir-doped Ca_3MnCoO_6, for instance) is currently underway. From the applied perspective, 5d elements are well known[25] to enhance technologically relevant properties (e.g. anisotropy and coercivity) of magnetic recording media. Studies of the model compounds with magnetic and nominally nonmagnetic elements could lead to advances in this field.

Many of the most exciting systems in solid-state physics belong to the class of 3d materials. Examples include cuprate and pnictide superconductors, and colossal magnetoresistance (CMR) manganites. Application of RXS on 3d K edges is a powerful technique for analyzing charge- and orbitally-ordered states in these materials[29]. Recent progress in the field allows the analysis of the electromagnetic multipole nature of the electronic states[30], leading to a much improved understanding of the physics involved. This has already led to reassessment of the nature of several well-known systems, such as an archetypal Mott insulator V_2O_3, in which the anapole and octupole contributions to the V ground state were established[31]. These advances clearly show that RXS studies on the K edges of the 3d elements will provide important insight into the physics of these ubiquitous materials. Many of the 3d systems also contain lanthanides, whose magnetism often controls their properties, as in multiferroic $REMnO_3$[27,28]. Disentangling the RE and 3d magnetism is crucial for understanding these systems, and RXS makes this separation possible.

In the area of applied materials, the high brightness of the beamline and intrinsic high-resolution of x-ray scattering will also provide a powerful probe of materials in an applied magnetic field. The magnetic field will be generated by a 1 Tesla magnet that mounts on the diffractometer (see Fig. 5), which is currently under development at NSLS, and could be used for studies of a variety of materials. Examples include magnetostrictives, which convert magnetic energy to mechanical energy and vice versa, and magnetoelectric materials, in which magnetization (polarization) is induced by an electric (magnetic) field. Other useful magnetic field-induced effects occur in magnetocaloric and magnetoresistive materials. In the former, structural transitions lie at the heart of the effect in many systems[32], while there is a growing consensus that inhomogeneities, which have unique structural signatures, drive the CMR effect[33]. Appreciable effects in many of these materials require fields larger than 1 Tesla, but technological requirements are driving the development of new materials that are functional at lower fields (e.g., magnetocaloric $Ni_{49}Mn_{39}Sb_{12}$[34]). For all of these classes of materials, high-resolution x-ray scattering in a magnetic field would be extremely useful: anisotropy, which affects the magnitude of some field-induced structural changes, can be probed in single crystals and

epitaxial films; in multiphase materials, powder diffraction can potentially clarify the field-induced structural behavior of individual phases; and in homogeneous polycrystalline materials, powder diffraction will enable structural characterization of novel field-induced phases.

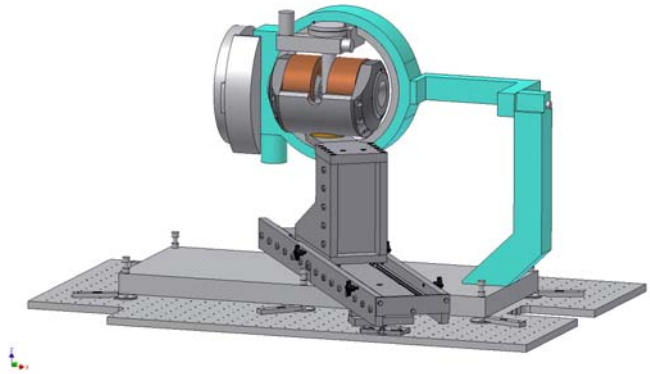


Figure 5. Conceptual design of a 1 Tesla magnet that mounts on a Huber diffractometer. Image is courtesy of George Rakowsky, Martin Woodle, and Richard Gambella.

A.4: Capabilities, uniqueness, and impact on field and community

Beamline: The 3-PW source will provide similar flux and ~20 times higher brightness than the current X20 and X22 beamlines. The choice of Si(111) or synthetic multilayers in a dual-bandpass fixed-exit monochromator will allow experimenters to use a high-resolution configuration for most diffraction measurements and high flux for most time-resolved measurements. The ability to quickly switch beam between the endstations and monochromator elements will permit rapid cycling between experiments and timely access for industry measurements. The ultimate goal is to be able to run automated RTAs on robotically changed samples overnight in endstation 1, and more thought-intensive experiments during the day in either endstation. This, along with remote access, will provide the most efficient use of the beamline, serve the largest community, and enable researchers to run experiments from their offices.

Endstation 1- RTA: The RTA chamber will be a unique tool, evolved from a highly successful endstation that has produced 28,000 measurements in the past 15 years at X20C. Users will choose between linear and area detectors. The techniques available will be *in-situ* real time XRD, XRR, SAXS, resistivity, and light scattering, for temperatures and kinetics of phase transformations, interfacial reactions, roughening, and agglomeration. There is no other dedicated endstation known world-wide for XRD, resistivity and light scattering measurements made simultaneously during RTA. Automated, remote running will make it even more useful and productive.

Endstation 2- XRD: A psi 2+4 Huber diffractometer, with offset phi and full chi circles, will be capable of holding a unique 1 Tesla magnet chamber, small environmental chambers, Displexes, and stages (including temperature, electrical, and stress). The user will have a choice of point, linear and area detectors. The choice of monochromator elements will allow for high resolution or high flux. Techniques will include high and medium-resolution XRD, resonant and magnetic scattering, GIXD, XRR, and high-throughput pole figures. The more standard X-ray techniques are extremely valuable to materials scientists in industry as well as academia. The resonant and magnetic scattering capabilities will be of great interest to solid state physicists.

A.5: The MPP beamline as a partner beamline with the In-Situ Resonant Scattering (ISR) beamline

The MPP and ISR beamlines are complementary and logical partners for occupying a sector of NSLS-II. Members of the two teams share common interests in materials growth and processing, materials development for microelectronics, solid state physics of complex materials, and the use of hard x-ray techniques for characterizing these systems both statically and under dynamical conditions *in-situ* and in real time. The MPP beamline emphasizes high-throughput and more standard techniques and fixed endstations. The ISR beamline extends to more intensive investigations of the growth and processing of materials, and determination of atomic structure at interfaces. These complementary beamlines cover the range of needs of this community: a 3PW source and endstations for continuation and evolution of existing X20, X21, and X22 NSLS programs, and an undulator source with 6-circle diffractometer and specialized growth chamber endstations to house the *in-situ* growth program at X21 and expand our capabilities to study emerging complex materials and processes for the 21st century. More details are given in Appendix 5.

A.6: The MPP beamline meeting industry needs through partnership with JPSI

IBM Research has been involved in the Joint Photon Sciences Institute from its inception in 2008. The industrial component of the Institute has a mission of enabling industrial research at both NSLS and NSLS-II. It serves as a gateway for access by seeking out and supporting industrial partners in the development of programs and instrumentation of interest to various sectors of industry. The MPP beamline clearly will serve many needs of the microelectronics industry, and IBM is eager to work with both the Light Sources Directorate and JPSI to fulfill this goal. A letter of support from JPSI can be found in Appendix 3.

B. Beamline Concept & Feasibility

The MPP beamline will use a 3mrad horizontal fan from a 3-pole wiggler source to maximize flux for the RTA endstation. A combination horizontal and vertical collimating mirror will be located upstream of the ratchet wall to capture the fan of radiation and enable the use of reasonably-sized downstream optics. A dual-bandpass monochromator (Si(111) and multilayers) with *in-situ*, easy switching of elements will follow. The energy ranges of the monochromator elements will be at least 4.9 – 14 keV (Si(111) for resonant scattering from the Ti to Ir edges) and 5 – 11 keV (multilayers for high flux and variable sample penetration). A toroidal focusing mirror for the XRD endstation will be placed at the 1:1 focusing position to maximize angular resolution, and a toroidal mirror for focusing beam in the RTA endstation will follow as closely as possible. The focused spot size at the sample will be less than 0.5 x 0.5 mm. The mirrors should be designed to move quickly and repeatably in and out of place so that beam can be switched between the two endstations in less than half an hour. In order to meet the goal of high throughput and efficient use, we would like to switch from running longer-term experiments in the XRD hutch during the day to running automated RTA measurements overnight, and then returning to the XRD experiment the following morning. This also requires that the monochromator element-switching and re-tuning be straightforward and repeatable to within several eV.

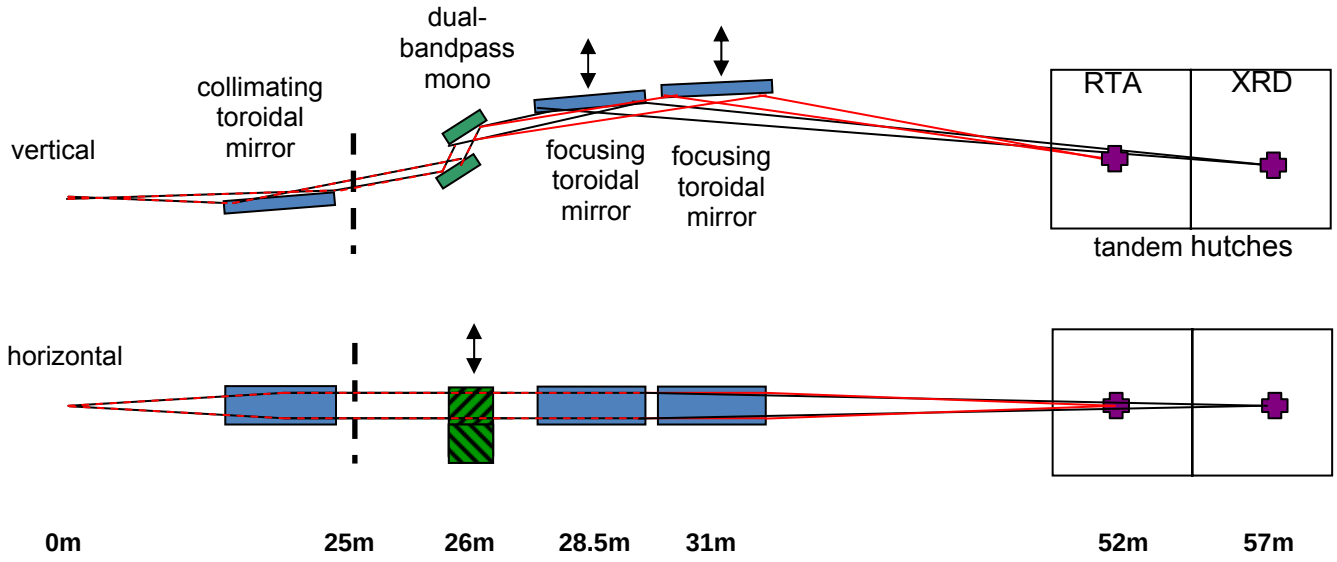


Figure 6. Beamline layout, not to scale.

Two endstations:

1. Six-circle (psi+2) Huber diffractometer with small chamber and Displex mounting capability, 1-Tesla magnet/chamber, high-dynamic-range point, linear and area detectors (we currently have APD, Hermes 640 pixel, and ADSC mixed-mode 256x513 pixel detectors available at X20 and X21).
2. *In-situ* real-time RTA, XRD, resistivity, HeNe laser light scattering. RTA capability from 0.1 to 35 ºC/sec ramps up to 1100ºC. Automated pump-down, purging, and flow-through of UHP He, N_2, or forming gas ambient. Robotic sample changing, remote access. Web-based sample database, sample tracking, automated routines for running measurements (start/end temperatures, ramp rate, hold times, scan type, detector angle(s), exposure times, total frames, attenuation, etc.). At X20C these are currently set using a Labview interface and "spec" and will be upgraded for interfacing with an Epics-controlled 640-pixel

Hermes linear detector within the next year. Immediate post-measurement analysis Matlab routines. Dedicated fast, high-dynamic-range linear and area detectors for RTA instrument.

C. Required Technical Advances

1) Rapid switching of beam between endstations and monochromator elements for minimum 8-hr duty cycle.
2) Robotic/automated control and remote operation of RTA endstation
3) Development of 1-Tesla magnet system, mountable on Huber diffractometer.

D. User Community and Demands

Historical Usage of Similar Beamlines

Demand for *in-situ* RTA endstation: IBM has been a PRT member at X20 since the startup of the NSLS x-ray ring and these beamlines have served as important characterization tools to complement our in-house capability. This is especially true of the unique *in-situ* RTA endstation at X20C. Over 28,000 measurements have been made on this endstation in the past 15 years. Currently, measurements are made by or for approximately 30 different scientists and engineers at IBM, mostly in the area of metal silicide process development and phase change materials characterization. In addition, we have academic collaborators whose research programs rely upon access to this endstation. They currently are Christophe Detavernier and students at Universiteit Gent, Patrick Dejardins and students at Ecole Polytechnique du Montreal, François Schiettekatte and students at University of Montreal, Darryl Butt and students from Boise State University, Santosh Kurinec and students from Rochester Institute of Technology, and Matthias Wuttig and students at the Technical University Aachen, Germany. General users with programs dependent on the endstation include Oana Malis and students at Purdue, Weigang Wang at Johns Hopkins, and John Smedley at BNL. In calendar year 2009, this endstation was used 115 days by IBM and academic collaborators, and 11 days by general users. In its present state, the endstation requires extensive training to use, and we expect the number of users to increase significantly once we have an efficient, automated endstation that can be controlled remotely, and have added XRR and SAXS capabilities. We also foresee new projects starting on this endstation and subsequently moving to the ISR beamline to take advantage of its enhanced capabilities.

Demand for 6-circle diffractometer endstation: This will serve the needs of users of x-ray diffraction beamlines for a wide range of studies. At the minimum, it will serve the programs of users from X20, X21, and X22, as described in Section A above. Over the past several beamtime request cycles, beamline X22C (diffraction) has had a subscription rate of 150%. In FY 2008-2009 the average number of unique users at X14A (diffraction) was 38, at X20A (diffraction) was 23, at X20C (in-situ) was 20, and at X21 (both) was 62. This endstation will also provide standard materials analysis techniques for new users from industry that use JPSI as a gateway to NSLS-II, and other members of the general user community.

Workshops and White papers: There have been several workshops held recently that address the scientific case and technical requirements for the research programs described in this proposal:

1. "Applications of Synchrotron-based Methods to Microelectronics Materials" organized by J. Jordan-Sweet and C. Lavoie, BNL, May 23, 2007. 30 attendees http://www.nsls.bnl.gov/newsroom/news/2007/06-Users_Meeting-ws9.htm
2. "Materials Science and Engineering Strategical Planning for NSLS and NSLS-II (92 attendees), Surface and Interface Science breakout session V, organized by J. Brock, R. Headrick, and K. Ludwig. http://www.nsls.bnl.gov/newsroom/events/workshops/2008/lsdp/mse/breakouts/breakout5_agenda.asp, white paper: http://www.bnl.gov/ls/workshops.asp
3. "Microelectronics Research Opportunities at the National Synchrotron Light Source," First JPSI workshop, organized by D. Fischer, J. Jordan-Sweet, C.-C. Kao, J. Wang, Albany Nanotech, March 23, 2009. 45 attendees. http://jpsi.bnl.gov/events/microelectronics/
4. "Integrated In-Situ and Resonant Hard X-ray Studies," organized by C. Nelson and K. Ludwig, joint workshop to develop MPP and ISR beamline proposals, May 27-28, 2010. 22 attendees. http://www.bnl.gov/nsls2/workshops/BeamlineDevelopment/Integrated%20In-Situ.asp

Industrial community needs: See section A1 and Fig 1. for IBM alliance/collaboration partners.

E. Proposal Team Expertise and Experience

Valery Kiryukhin: Valery is an Associate Professor at Physics Dept., Rutgers University. He has more that 15 years experience with synchrotron x-ray scattering techniques, including resonant x-ray scattering (elastic and inelastic), and scattering in high magnetic fields. His main interests involve solid-state systems with strong electronic correlations, quantum magnetism, and nanoparticle systems. He has performed numerous experiments at the NSLS (X22, X21, X20, X1) and at the APS. He was a PRT member at X22C, a representative at the NSLS UEC, and Proposal Review Panel member at the NSLS and APS.

Christie Nelson: Christie is a Physicist at the NSLS, and is currently the spokesperson for the X21 facility beamline and the X16B and X22A diagnostics and instrumentation beamlines. In her 17 years of experience with synchrotron radiation, she has carried out research at SRS, APS, PETRA, LNLS, and the ESRF, in addition to the NSLS. Christie's research interests lie in the fields of correlated electron systems and magnetic materials, and she primarily uses x-ray scattering techniques to probe their complex properties. The recent focus of her work has been on multiferroic materials.

IBM and Collaborators: IBM (J. Jordan-Sweet, C. Lavoie, C. Murray, and C. Noyan (Columbia U./IBM Research Consultant since 2004)) has been a leader in industrial synchrotron research for over 26 years, starting with the design and building of lithography, photoelectron spectroscopy, and x-ray diffraction beamlines at the NSLS, followed by regular operations and support. In the hard x-ray field, we developed the first microdiffraction capability at NSLS and a unique endstation for simultaneous *in-situ* XRD, light scattering and resistivity measurement during rapid thermal annealing of thin films and nanopatterned samples. Our researchers have also worked through the peer-reviewed general user proposal systems at NSLS, SSRL, APS, and ALS. In collaboration with academia, we have developed rapid analysis methods for time-resolved data (rapid thermal annealing and isothermal holds) and texture analysis. Particular strengths of each team member are:

Jean Jordan-Sweet: Jean is a research staff member of the IBM T.J. Watson Research Center, with over 26 years experience as a beamline scientist at NSLS (2 years at U8, 24 years at X20). She is spokesperson for the X20 beamlines and assisted in the design and building of X20B, in the development of the first microdiffraction endstation at NSLS (headed by Cev Noyan), and in the evolution of the unique *in-situ*, three-probe time-resolved RTA endstation at X20C. She is practiced in many hard x-ray techniques, including HRXRD, GIXD, XRR, texture, microdiffraction, and *in-situ* XRD, and has some experience with EXAFS, XPS, and SAXS.

Christian Lavoie: Christian, an IBM Research Staff Member, has worked with synchrotron radiation extensively over 15 years, for *in-situ* XRD characterization during annealing of thin films and arrays of nanostructures as well as for *ex-situ* measurements using x-ray reflectivity. Within IBM, he has been responsible for the design and upgrades of a unique *in-situ* diffraction end-station and is currently leading the materials research needed for building contacts to state-of-the-art and emerging microelectronic devices.

Conal Murray: Conal Murray has focused on applying micromechanical models to describe the behavior of semiconductor structures and experimentally validating these models using X-ray diffraction-based techniques. Recent projects include the detection of strain within silicon-on-insulator (SOI) channels due to embedded source / drain stressors and the investigation of stress gradients within Cu metallization induced by capping layers. He has conducted experiments at several synchrotron facilities (NSLS, APS, ALS, SSRL, CHESS) over the past 15 years. He is a frequent user of the microbeam (2-ID-D) and Hard X-ray Nanoprobe (26ID) beamlines, where he has mapped deformation and strain in advanced microelectronic structures. He has investigated the evolution of texture, stress and microstructure in semiconductor metallization and silicide materials. He has also created boundary element model (BEM) software to predict the mechanical behavior of thin film / composite structures and implemented anisotropic elasticity formulations and Eshelby inclusion methods to the study of strained Si systems.

I. Cev Noyan: Expertise in *x-ray and neutron diffraction physics*: first-principles modeling of diffraction peaks, microdiffraction techniques, synchrotron end-station design and construction; *solid mechanics and micromechanics*; *nondestructive testing and stress/strain analysis*. Cev had been involved in synchrotron research and instrumentation development for over 25 years.

F. Suggestions for BAT Membership

We suggest having the BDP Team serve as the BAT membership. We will depend on the expertise of NSLS and NSLS-II staff for help in developing the optimal design and layout for the beamline. Contact information can be found on the first page.

G. Funding and Management

IBM has extensive experience in the design, construction and operation of an endstation at the NSLS for the *in-situ*, temperature and time-resolved technique described above, and is interested in discussing with NSLS-II a collaboration for the construction, commissioning, operation of, and access to, the new upgraded endstation for the MPP beamline.

Appendices:

1. **References**
2. **Biographical sketches**
3. **Letters of support**
4. **Students whose theses included work performed at X20 beamlines**
5. **MPP as partner beamline to ISR beamline**

Appendix 1. References

1. ITRS Roadmap: http://www.itrs.net/Links/2009ITRS/Home2009.htm
2. J.M.E. Harper *et al*., *Ann. Rev. Mater. Sci*. **30**, 523 (2000); C. Lavoie *et al*., *Microelectron. Eng*. **70**, 144 (2003).
3. L.A. Clevenger *et al*., *J. Mater. Res*. **10**, 2355 (1995); R. Roy *et al*., *Appl. Phys. Lett*. **66**(14), 1732 (1995); C. Cabral, Jr. *et al*., *Appl. Phys. Lett*. **71**, 3531 (1997).
4. C. Lavoie *et al*., J. Electron. Mater. **31**, 597 (2002).
5. C. Lavoie *et al*., *Microelectron. Eng*. **83**, 2042 (2006); P. Besser *et al*., *ECS Transactions* **13**(1) 377 (2008).
6. S. Raoux *et al*., *IBM J. Res. Devel*. **52**, 465 (2008); *Microelectron. Eng*. **85**, 2330 (2008).
7. S. Raoux, *et al*., *J. Appl. Phys*. **103**, 114310 (2008); *J. Appl. Phys*. **102**, 094305 (2007).
8. C. Cabral, Jr. *et al*., *Thin Solid Films*, **397**, 194 (2001); H. Kim *et al*, *J. Appl. Phys*. **95**, 5848 (2004) and **98**, 014308 (2005);
9. Forest, Louis. Soudures sans-plomb pour la microelectronique, Proquest Dissertations And Theses 2008. Section 1105, Part 0794 192 pages; [M.Sc.A. dissertation].Canada: Ecole Polytechnique, Montreal (Canada); 2008. Publication Number: AAT MR41556.K; Chen, N. Tamura, M. Kunz, K.N. Tu, Y-S Lai, *J. Appl. Phys*. **106**, 023502 (2009).
10. W.P. Leroy *et al*., *J. Appl. Phys*. **99**, 063704 (2006); J. Smedley, *MRS proceedings*, submitted.
11. C. Detavernier *et al*., *Nature* **426**, 641 (2003).
12. C. Detavernier *et al*., *Appl. Phys. Lett*. **84**, 3549 (2004); D. Deduytsche *et al*., *J. Appl. Phys*. **101**, 044508 (2007); C. Van Bockstael *et al*., *J. Appl. Phys*. **104**, 053510 (2008).
13. C.E. Murray *et al*., *Appl. Phys. Lett*. **93**, 221901 (2008).
14. L. Edge et al., *Appl. Phys. Lett*., submitted.
15. S. Raoux *et al*., *J. Appl. Phys*. **101**, 044909 (2007).
16. M.L. Green *et al*., J. Appl. Phys. **105**, 103522 2009).
17. B.J. Kim *et al*., *Science* **323**, 1329 (2009).
18. For a review, see M.Z. Hasan and C.L. Kane, preprint arxiv:1002.3895, http://arxiv.org/abs/1002.3895.
19. A. Shitade *et al*., *Phys. Rev. Lett*. **102**, 256403 (2009).
20. G. Jackeli and G. Khaliullin, *Phys. Rev. Lett*. **102**, 017205 (2009).
21. I. Nagai et al., *J. Phys.: Condens. Matter* **19**, 136214 (2007).
22. D.I. Khomskii and T. Mizokawa, *Phys. Rev. Lett*. **94**, 156402 (2005).
23. G. Khaliullin and M. Haverkort, unpublished.
24. S-W. Cheong and M. Mostovoy, *Nature Mater*. **6**, 13 (2007).
25. W.B. Zeper *et al*., *J. Appl. Phys*. **65**, 4971 (1989).
26. D. Mannix *et al*., *Phys. Rev. Lett*. **86**, 4128 (2001).
27. B. Lorenz *et al*., *Phys. Rev. B* **76,** 104405 (2007).
28. T. Lottermoser *et al*., *Nature* **430**, 541 (2004).
29. G. Subias *et al*., *J. Physics*: *Conference Series* **190**, 012085 (2009).
30. S. DiMatteo *et al*., *Phys. Rev. B* **72**, 144406 (2005).
31. S. Lovesey *et al*., *Phys. Rev. B* **75**, 014409 (2007).
32. K.A. Gschneidner, V.K. Pecharsky, and A.O. Tsokol, *Rep. Prog. Phys*. **68**, 1479 (2005).
33. E. Dagotto, *New J. Phys*. **7**, 67 (2005).
34. W.J. Feng *et al*., *J. Phys. D : Appl. Phys*. **42**, 125003 (2009).

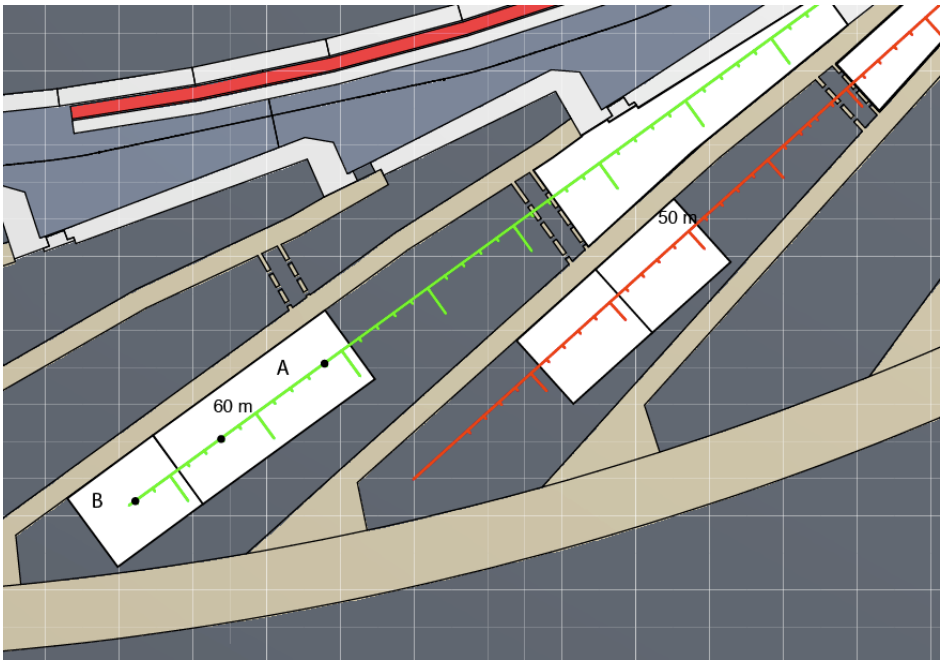
Appendix 5. MPP as partner beamline to ISR beamline

Karl Ludwig is leading a PDT proposing an undulator-based beamline for **Integrated *In-situ* and Resonant Hard X-ray Studies (ISR)** that will utilize the source's high brilliance to enable studies of the physics of emerging materials, addressing several key DOE Grand Challenges: "How do we characterize and control matter away – especially very far away – from equilibrium?", "How do remarkable properties of matter emerge from complex correlations of the atomic or electronic constituents and how can we control these properties?", and "How do we design and perfect atom- and energy-efficient synthesis of revolutionary new forms of matter with tailored properties?" Addressing these complex materials problems requires not just a single approach, but rather a flexible and broad range of capabilities that can be utilized synergistically. ISR will provide NSLS-II with a beamline that takes full advantage of the unique NSLS-II source characteristics coupled with the latest technique advances (polarization, resonance, coherence) to create a ***world-leading, next-generation tender/hard x-ray diffraction facility***. It would form a natural partner to the MPP program intellectually, and in practical use of the neighboring floor space (see sector layout in next page).

The PDT for the ISR beamline proposal is:

Karl Ludwig (Spokesperson): Professor of Physics, Boston University
Andrei Fluerasu: Associate Physicist, NSLS-II, BNL
Randall Headrick: Professor of Physics, University of Vermont
John Hill: X-ray Scattering Group Leader, BNL-Condensed Matter Physics and Materials Science
Jean Jordan-Sweet: Research Staff Member, IBM T.J. Watson Research Center
Valery Kiryukhin: Professor of Physics, Rutgers University
Paul Lyman: Professor of Physics; University of Wisconsin – Milwaukee
Christie Nelson: Physicist, NSLS, BNL
Ron Pindak: Physical and Chemical Sciences Division Head, NSLS, BNL

If the MPP and ISR beamlines were not constructed, the impact on NSLS-II would be significant:
1. NSLS-II would not be able to provide researchers with the capability of providing atomic-level structural information including magnetization and chemical composition of buried interfaces, which is critical information to develop a first principles understanding of the emergent new physical phenomena that occur at interfaces. BNL and Stony Brook University would, hence, not be able to take full advantage of their investments in atomic level growth facilities such as those developed by Ivan Bozovic (MBE at BNL) or Matthew Dawber (PLD at SBU).
2. NSLS-II would not be able to provide researchers the capability to study and understand the non-equilibrium kinetics involved in processes being used by industrial labs to fabricate products to meet the DOE energy challenges. This was one of the primary needs emphasized by industrial participants in the JPSI workshops on microelectronics and excitonic photovoltaic materials and devices.
3. NSLS-II would be lacking the tender/hard x-ray resonant scattering results needed to achieve a complete structural refinement of the powder diffraction data from highly complex materials such as nano-composites that will be measured on the NSLS-II Powder Diffraction Project Beamline.
4. For IBM researchers, the loss of access to their *in-situ* set-up at a nearby facility like NSLS-II would impact timely development of materials and processes for next-generation technologies such as silicide contacts and universal memory.



Above: Schematic of sector layout. The ISR canted undulator beamline is the inboard line, shown in green. It incorporates a first optical enclosure, and two endstations: Endstation A with two diffractometer positions and Endstation B. The 3PW MPP beamline is the outboard line, shown in red. It has a first optical enclosure and a two endstations. The area behind the 3PW endstation would potentially be available for future development, as described in Appendix B of the ISR proposal.