APPLICATIONS OF NUCLEAR ANALYTICAL METHODS FOR HIGH TECH INDUSTRY

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1. INTRODUCTION

Silicon based semiconductor chip manufacturing is a worldwide high technology industry with numerous measurement issues. One of the major concerns in the semiconductor manufacturing is contamination such as the trace metal impurities. This concern is vividly illustrated by the fact that the manufacturing in this industry is done in ultra clean environment where the entire manufacturing facility or "Fab" is a clean room facility or each and every manufacturing tool is enclosed in a mini-environment Although semiconductor devices are fabricated on the surface of the Si wafers contamination in the bulk material is a major concern. Nuclear methods of analysis are uniquely suited for the contamination analysis in such a matrix.

2. OPPORTUNITIES FOR NUCLEAR ANALYTICAL METHODS

Nuclear analytical methods can be used to provide many essential data needed for the chip manufacturing process technology both for R & D and manufacturing operations.

Neutron activation can provide trace impurities analysis at ultra low levels. The favorable neutron activation parameters for Si as a matrix make such low level measurements possible. First Si leads to ^{31}Si which has a 2.6 hour half life so that matrix radioactivity decays quickly to virtually nothing creating an excellent low background condition. The impurities of interest are the first row transition metals, which typically have much longer half lives. NAA has high sensitivity for these elements. Detection limits for some elements are listed below in Table 1. These limits can be achieved by using reactor core irradiation at high flux positions. Turnaround time for such analysis for a set of samples can be up to 2 weeks since multiple counts may be necessary to include all the elements listed. High resolution gamma spectroscopy with good shielding is necessary to obtain these limits.

TABLE 1. TYPICAL DETECTION LIMITS IN SILICON WAFER

Elements	Minimum concentration for detection (cm^{-2})
Fe, Ni	8×10^{10}
Cr, Mn, Co, Sc	1×10^{9}
Cu, Ag, Zn	$1–5\times10^{10}$
Au	1×10^{7}
Ta, Th, La, Eu	1×10^{9}
As, Sb, U	5×10^{9}
Na, K	$1–5\times10^{10}$

However non-nuclear methods such as TXRF and VPD-ICP/MS can also make such low level measurements. The disadvantage of NAA is that typically it would take 2 weeks to obtain the results while both TXRF and VPD can provide data in less than a day. Furthermore

TXRF is automated, and can be placed inside the Fab where in-line measurements can be done non-destructively. VPD is highly quantitative and NIST traceable standards are available. A major weakness of TXRF, and VPD is that data collected is from the surface of the wafer only. In case of TXRF the analysis depth is about few tens of nanometers, while VPD data is limited to the native oxide only. Any subsurface or bulk impurities would escape detection by these methods. This is where opportunities for NAA exist to complement the surface analysis by the TXRF, and VPD with bulk analysis results thus providing complete picture for trace metal contamination.

In fact for bulk analysis NAA is the preferred method and in some cases only method creating an opportunity to support the high tech manufacturing field. The high sensitivity of NAA for bulk measurements provides a unique solution to the semiconductor industry. Several types of samples can be analyzed for bulk impurities. Most notably Si wafers, SiC, graphite, quartz, and Si_3N_4 are among the most widely used material needing such bulk analysis. Samples of the above type cannot be analyzed with conventional methods such as ICP/MS since digestion of these materials leave high levels of Si in solution that must be diluted in order to run through the mass spectrometer. This necessary dilution makes the detection limits not attractive.

The analysis of Cu deserves special mention since it plays a pivotal role in chip manufacturing. The interconnect metal for semiconductor devices is shifting from Al to Cu for higher conductivity of the latter. However Cu has high diffusivity in Si and with modest temperature Cu can move from the backside of the wafer to the front or the polished side where the devices are fabricated. The Cu contamination control therefore is a big challenge, and monitoring Cu levels in the Fab is an on-going program. Since bulk levels of Cu must be monitored NAA becomes the method of choice for this very important measurement needs for the semiconductor industry.

Another opportunity is in the implant area of the process technology. For example As is used as the n-type dopant for Si. It is most often implanted into the Si with specific energy, and dose. After implantation, a temperature anneal is done typically ~1000°C to activate the dopant atoms, in this case As atoms, where the As atoms substitute in the Si crystal lattice. There are two issues that need to be monitored. For a manufacturing Fab there are multiple implanters that need to be matched with respect to the dose, hence total As analysis is needed. Secondly since As is volatile, it is important to determine after anneal at high temperature whether there a loss of Arsenic due to diffusion. NAA can provide an excellent answer to these very important questions and help set up process parameters needed for the successful fabrication of the devices.

There are unique environmental analysis needs in the semiconductor industry. One such need has been just created due to the Restrictions on Hazardous Substances (ROHS) ordinance agreed to in the Europe Union. The EU after 1 July 2006 will require that all electronic products and components among other things be essentially free of metals such as lead, cadmium, and mercury.

NAA has the advantage in measuring Hg quantitatively while the non-nuclear methods have serious problems. NAA method developed for this purpose is a great opportunity to meet the needs of regulatory compliance.

3. NEUTRON DEPTH PROFILE

In addition to the above NAA opportunities there are other nuclear methods that can provide elegant solutions to the high tech industry. Neutron depth profiling (NDP) is a special technique that has unique applications in the Fab process technology.

The most widely used p-type dopant for Si is boron, and the dose and the profile of boron is crucial for the functioning of the fabricated devices just like the case of As mentioned above. Typically secondary ion mass spectrometry (SIMS) is used to provide the information about the boron. However a standard is needed for such measurements, and SIMS is very matrix sensitive. In fact SIMS is not reliable at all for measurements across an interface such as oxide–Si. This is because the SIMS yield changes uncontrollably across any interface. NDP is neutron based and provides answers to these problems faced by SIMS. In this method implanted boron (^{10}B) is exposed to thermal neutron beam in an evacuated chamber. The fission reaction between ^{10}B and thermal neutrons produces monoenergetic alpha particles of 1.47 MeV that are emitted isotropically. A surface barrier detector can measure the energy of the alpha particles, and can construct from the energy loss spectrum the boron implant profile. In addition it can also provide dose of the boron implant by integrating the area under the curve.

The advantage of NDP is that one can depth profile boron across an interface since neutron penetration is not sensitive to oxide/Si matrix. A true distribution of boron can be unambiguously measured. NDP can also generate standard samples that can be used in SIMS measurements to provide quantitative results. NDP is also advantageously used for borophosphosilcate glass (BPSG) analysis where boron concentration is critically monitored for process technology. Measurement of boron in BPSG by SIMS is at best difficult because of the charging issues associated with the thick oxide layer.

4. PROMPT GAMMA FOR H ANALYSIS

A lot of the thin films that are deposited for device fabrication are oxides, and nitrides of Si. They are deposited using plasma enhanced chemical vapor deposition (PECVD) or low pressure chemical vapor deposition (LPCVD) techniques in which the precursor for Si is the Silane gas, SiH_4. This results in incorporation of Hydrogen in these films. Measurement of hydrogen in thin films of a few hundred nanometers is often needed to set up a deposition recipe for these films. Although hydrogen in these films can be measured using SIMS a standard is needed for quantitative results. For this purpose nuclear method of prompt gamma analysis can provide total hydrogen concentrations in these films. Prompt gamma is a robust measurement that can analyze films of different compositions such as SiO_2, SiON, Si_3N_4, etc.

4.1. Soft error issues

Semiconductor devices containing BPSG layers have a unique problem with cosmic ray neutrons. These neutrons can undergo fission reaction with ^{10}B in the BPSG layer and generate energetic alpha particles of 1.47 MeV. These charged particles will penetrate into the active area of the device, e.g. transistor or capacitor and cause single event upsets. For example in the memory array the charge stored can be discharged making the bit oscillate between zero and one. Such undesirable bit flip known as soft error, and semiconductor manufacturers would like to limit such soft error rate (SER) to a minimum. Opportunities exist for nuclear facilities to provide neutron flux for testing device configuration to evaluate a device design with respect to its resistance to SER. This is particularly important for the mobile computer that may operate at high altitude for example in an airplane in flight. Design alternatives can be worked out using nuclear methods of evaluation.

5. PB BUMP TECHNOLOGY

Many devices are being made with Pb bump technology where essentially a micro Pb solder replaces the traditional ball bonding with Au wire. Such a chip often contains a high density of Pb bumps. One issue with this technology is the possible contamination of Pb with radioactive ^{210}Pb which has a half life of 22 years. The radioisotopes eventually emit alpha particles which can penetrate the thin metal layers and cause bit flip in the sensitive area of the device. Considerable design efforts have been devoted to offset the problem caused by this phenomenon. However ultra low radioactivity Pb is a better solution even though it is costly one often times at 10x the expense. Manufacturer of these C4, the given name to Pb bump technology in the industry, devices need low level radioactivity measurements to evaluate the quality of the Pb being used for this purpose. A nuclear facility with low background counting set up can provide this service to the industry.

6. INDUSTRIAL CUSTOMER NEEDS AND REQUIREMENTS

Manufacturing industries have demanding needs in the metrology, and analytical measurements. This is driven by the need for improvements of the products and efficient process technology. For example in semiconductor industry to support a manufacturing operation a well-equipped laboratory is essential. Such a laboratory may contain analytical tools such as XPS, Auger for surface analysis; SIMS for depth profiles of dopants, SEM, TEM for imaging and cross sections; TXRF, and VPD/ICPMS for surface contamination analysis; XRD for orientation and texture while Raman, FTIR, EDX for defect analysis. In addition there are metrology tool on line to gather data for critical dimension (CD) and thickness. However the bulk impurities analysis of the Si wafer substrate cannot be addressed by any of the above techniques. This is a gap which can be ideally fulfilled by the NATs. High sensitivity NAA is an excellent choice to provide this critical data for the entire semiconductor manufacturing community. Bulk analysis of other materials such as SiC, quartz, graphite liners and silicon nitride can also be accomplished by NAA. The need for such analysis in the semiconductor industry is a daily phenomenon and currently not being met adequately. Demand for such analysis worldwide is high, and NAA providers can develop a niche market for this service.

Another important example of the unique applications of NATs in the semiconductor industry is the analysis of dopants across an interfacial boundary which is a frequently needed analysis in the chip manufacturing. Typically SIMS is used for dopant analysis. Incidentally several commercial labs are set up just to provide SIMS data to the semiconductor manufacturing customers. However interfacial analysis by SIMS is not reliable because of the uncertainty inherent to the technique for the interfaces. NATs such as NDP is uniquely suited for the analysis of the boron across an interfacial boundary. Because of the insensitivity of the neutron to a matrix such as oxide/Si the profile of boron can be unambiguously obtained by NDP across such an interface. Chemical etching post neutron irradiation can provide such interfacial data for other dopants such as P, As, In, etc. These high priority demands in the industry can be met by the NATs, and there exists a potential commercial market.

Outside of the semiconductor industry following is a short compilation of the unique applications of NATs in the industry. This is only an attempt to list a few relevant usage of the NATs and actual needs are much more widespread.

— Analysis of trace oxygen in Steel, and petroleum processing. Such direct measurement of oxygen is only provided by NAT; in this case the 14 MeV fast neutron activation analysis;

— Hydrogen analysis in the Ti metal industry for aerospace. PGNAA is a highly quantitative method that is unmatched by any other technique;
— Halogens and metals in the polymer industry can be uniquely addressed by NATs. This is evidenced by the investment made by Dow Chemicals to install a research reactor for their own use at their Midland manufacturing facility in Michigan;
— Industries that produce materials such as ceramics, graphite, and other highly refractory or insoluble materials have demands for NATs. Should the conventional methods of chemical dissolution be unavailable, NATs can meet the trace analysis demands for, e.g., AlN, glasses, etc.; and
— Impurities in emerging nanomaterials, e.g., for carbon nanotubes, NAA is best suited for trace impurities analysis in this field.

There is a clear demand for NATs in the various industries, and a potential commercial market can be developed in order to satisfy such important industrial needs. However the industrial customers have requirements which must be met not only for technical contents but also for all other logistics such as delivery on time, and proper non-disclosure agreements. For a successful commercial opportunity the infrastructures must be built to have business like interaction between the service provider, and the industry. Industrial customers would require priority, confidentiality, and on-time delivery. Service providers must show long term commitment so that industrial customer can rely and plan future manufacturing, but a quality system is required.

Industry on the other hand must allocate annual budget items so that service providers can make investments for upgrading facilities, and tools. Such investment on the part of the provider is critical in order to meet the increasing demand of the manufacturing industry.

7. CONCLUSION

Many opportunities in the semiconductor manufacturing field exist for the nuclear methods to provide support services. Contamination analysis by NAA, depth profiles by NDP and prompt gamma analysis of H in thin films are a few examples. These needs are on-going and require commitment from the lab so that a manufacturing operation can rely on the delivery of these services when required.