INDUSTRIAL APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS

XA0101174

T.Z. Hossain
AMD, Inc.,
Austin, Texas, United States of America

Abstract. Neutron activation analysis has been widely used in the industry and over the years played a key role in the development of manufacturing process as well as monitoring of the process flow. In this context NAA has been utilized both in R &D, and in the factory as a flexible analytical tool. It has been used successfully in numerous industries including broad categories such as Chemical, Pharmaceutical, Mining, Photographic, Oil and Gas, Automobile, Defense, Semiconductor and Electronic industries. Dow Chemical owns and operates a research reactor for analytical measurements of samples generated in both R & D, and manufacturing area in its plant in Midland, Michigan. Although most industries do not have reactors on their campus but use an off site reactor regularly, and often have in-house neutron sources such as a ^{252}Cf used primarily for NAA. In most industrial materials analysis laboratory NAA is part of a number of analytical techniques such as ICP-MS, AA, SIMS, FTIR, XRF, TXRF etc. Analysis of complex industrial samples may require data from each of these methods to provide a clear picture of the materials issues involved. With the improvement of classical analytical techniques, and the introduction of new techniques e.g. TXRF the role of NAA continues to be a key bench mark technique that provides accurate and reliable data. The strength of the NAA in bulk analysis is balanced by its weakness in providing surface sensitive or spatially resolved analysis as is required by many applications.

1. INTRODUCTION

In the following pages first hand experiences of using NAA as a part of a larger analytical laboratory consisting of many other methods are described. The applications given below were in the Photographic, Chemical, and Semiconductor manufacturing industries. In each case NAA was a critical complementary technique needed for successful resolution of manufacturing problems.

2. APPLICATIONS IN PHOTOGRAPHIC INDUSTRY

2.1. Precise doping of silver halide crystals

A very important consideration in the manufacturing of the photographic films is the precise doping of the silver halide crystals with ultra low level impurities such as Ir, Rh, and Au. Typical levels are in the low ppb range, however the performance of the films such as speed or sharpness depend on maintaining a precise doping level in the high volume manufacturing. Analysis of these dopants was found to be best performed by NAA with a pre-irradiation separation chemistry. In a comparison of many techniques such as AA, ICP-MS, XRF, and others, NAA provided the most repeatable and reliable data over a long period of time (> 2 years). The high thermal neutron cross sections of these dopants made NAA a very sensitive technique, and analysis at ppb level could be performed with great precision. The method was susceptible to very few extraneous factors, and immune from a number of background related abnormalities. Although a pre-irradiation separation was necessary to avoid activating long lived Ag or intense halide radioactivities the final result of measuring Ir count rates proved to be highly sensitive, and precise. A shift in the manufacturing process due to dopant variation could be monitored, and reliable non-varying photographic films can be produced over a product life cycle. In this case NAA turned out to be a vital technique for the successful manufacturing of a high volume product sold through out the world.

A related monitoring application, although did not require the use of the reactor is worth mentioning. Chemically most photographic films are mixed halides e.g. AgBrCl, AgBrI etc. The mole ratio of the halides determines the sensitivity of the color films. Using an in-house ^{252}Cf neutron source the halide ratio in these mixed halides can be readily, and reliably measured. Conventional techniques requiring dissolution of these halides resulted in very

poor quality data not suitable for controlling a manufacturing process. Yet NAA provides such an easy and elegant analysis of this key industrial process proving to be an excellent application of the technique in the industry.

2.2. Impurities in Gelatin

Gelatin used as the emulsion in which Ag halides are dispersed is required to be high purity. Presence of trace impurities such as Hg, Se can be highly inhibitive to the photoactive processes and latent image formation. A reactor based NAA of the gelatin was found to provide superior quality trace analytical data when compared with other techniques such as hydride generation, and cold vapor atomic absorption.

3. APPLICATIONS IN THE CHEMICAL INDUSTRY

3.1. Iodine in polymers

Bulk chemical manufacturing often require final product to have low level impurities. For example a bulk hydrocarbon polymer may not contain any halogen impurities. In one such application where the final polymer used in the automobile industry needed to be essentially free of iodine. Iodine being volatile was difficult to analyze by conventional dissolution methods at low level. The short half life and the good thermal neutron cross section made the detection of iodine by NAA in polymers a sensitive, and reliable analysis. The level of iodine in this high volume polymer production was monitored by NAA over a long period time. Samples from the production line were collected, and periodically sent to off site reactor for accurate analysis of iodine. Using this logistic a control chart was made for the process, and maintained for the manufacturing of the polymer.

3.2. Metallic catalysts remainders in high volume polymers

A second example in this industry also involves production of high volume polymers e.g. polyester. Often time metallic catalysts are used in the manufacturing process, and are not desirable to be present as impurities in the final product. A Mn or Sb contamination can be easily picked up in the polyester or PET (polyethylene terephthalate) manufacturing. These impurities can be readily detected by NAA at a low ppm level, Methods such as XRF can be used for the metallic impurities analysis for thin polymer films. However XRF sensitivity often is not good enough to use in the low level monitoring applications. Catalytic impurities such as Sb being a toxic metal need to be controlled, particularly when the product (e.g. PET) is used in food related applications such as the beverage containers. NAA is ideal for monitoring the Sb levels resulting from the use of the Sb oxide catalyst in the manufacture of PET polymers.

3.3. Benchmarking of other methods

Use of NAA as a bench mark technique for calibration of other methods is widely practiced. In many suitable applications NAA data is highly quantitative. Since it is free from cross contamination from reagents or is not easily affected by absorption (both neutrons, and gamma rays are penetrating radiation) the analysis is robust and reliable. This makes NAA very suitable for bench marking conventional methods such as XRF, AA, ICP, etc. The role of bench marking is not limited to chemical industry alone. NAA bench marking has been used in other industries as well.

4. SEMICONDUCTOR INDUSTRY APPLICATIONS

4.1. Trace impurities in high purity Si

In the production of high purity Si needed for VLSI manufacturing NAA was very effective for the whole semiconductor industry. Trace impurities in starting Si is required to be below sub ppb level. Monitoring of bulk impurities in Si introduced during the crystal growth process is best done by using NAA. The matrix is very favorable since the half life of the radioactive Si is short (i.e. ^{31}Si, $t_{1/2}$ 2.6 hours), and the elements of interest (transition metals) have long half lives a very high sensitivity analysis can be obtained. Detection limits for some elements such as Au (highly undesirable in semiconductor Si) can be in the range of few parts per trillion. Bulk analysis by NAA has established the quality of Si used in the semiconductor manufacturing today.

A relatively new technique, Total reflection X-ray Fluorescence (TRXRF) has been widely used for trace level monitoring of surface impurities in the Si wafers. TRXRF cannot measure bulk impurities since it is designed as a surface technique. However the detection levels are in the range of $-2 \cdot 10^9$ atoms.cm^{-2}. Advantages of the TRXRF technique is the rapid turnaround time, and that the instrument can be placed inside the fabrication floor for automated analysis by semiskilled technician.

4.2. Contamination control in VLSI manufacturing

Cross contamination which is a very big issue in VLSI manufacturing can be monitored effectively by NAA. The key for this type of analysis is to have the low detection limit since semiconductor devices are susceptible to small contamination. Often times samples are clean room quality rags or wipes with irregular shape so that only a bulk analysis done non-destructively is reliable. Most other techniques suffer from sample preparation for this low level analysis. The elements of interest in this case are Co (cobalt silicide process), Cu (copper metallization), etc. NAA for these analysis can provide higher quality data compared to ICP-MS. However the turnaround time for ICP-MS is much better, and prove to be more important.

4.3. Bulk analysis of quartz

Bulk analysis of the quartz used in the furnace for Si wafer processing is another example where NAA is highly suitable, and is routinely done either by the chip manufacturers or their quartz supplier. High sensitivity and low detection limits are obtained in this matrix with little sample preparation. The competing techniques of ICP-MS and TRXRF are not as convenient, particularly TRXRF yields only surface concentrations. Use of high purity quartz is essential in the high volume chip manufacturing where low level transition metal contamination can be a disaster and lead to non functional dies. Other materials that need bulk analysis in semiconductor industry include SiC (used in vertical furnaces), various plastic packaging materials for U, and Th (precursors of alpha particle emitters), aluminium metal (used as interconnect), and thin films of silicon dioxides, Ti, TiN, W etc. However for thin film cases alternate methods such as the TRXRF provide rapid and reliable analysis, and is often the method of choice.

4.4. Use of other nuclear analytical methods

It is important to note a few important analysis for the semiconductor industry that are done using a reactor neutron source but are not neutron activation analysis by definition. These are neutron depth profiling (NDP), and prompt gamma activation analysis (PGNAA). Both of

these methods are closely related to NAA, and have similar materials analysis considerations. NDP has been uniquely used for depth profiling boron in thin CVD (Chemical Vapor Deposition) silicon oxide films (- μm) such as BSG (borosilicate glass), BPSG (borophosphosilicate glass), and BPTEOS (borophospho tetraethyl ortho silicate) films. Analysis require a neutron beam, and data is collected while the samples are under neutron irradiation. NDP can depth profile a few micrometer thick films, and is particularly suitable for the semiconductor industry since devices are manufactured as thin films on Si wafers. The boron depth profiling is also widely done using SIMS (secondary ion mass spectrometry). However NDP can provide highly quantitative data, and accurate profile free of interfacial yield problems that plague the SIMS methodology. Anytime a depth profile across an interface such as the SiO_2/Si is needed NDP has an advantage since there is no direct effect of the interface in the neutron irradiation of the boron. SIMS on the other hand has different sputtering yield across the interface and results in a profile that need to be carefully interpreted. The limitations of NDP is also its strength, i.e. only a few elements can be analyzed by this technique e.g. B, N, O (labeled with ^{17}O isotope).

The second related method, PGNAA is also very important in the semiconductor industry for measuring bulk hydrogen content of thin films produced in CVD process. Many CVD process use organo metallic gases such as TEOS or silane for silicon oxide films, TDNMT (tetrakis dimethyl amine Titanate) for CVD TiN films etc. The final thin films contain hydrogen often at a level of up to 40–50 atomic%. Hydrogen contents of these films can have significant effect on the device performance (e.g. hot carrier injection) and therefore need to be taken into account in a manufacturing process. PGNAA can measure the bulk hydrogen in CVD films quantitatively, and provide a bench mark for many of these processes. Other techniques such as FTIR and nuclear reaction analysis have been used to obtain chemical nature of hydrogen, and the distribution of hydrogen respectively. These measurements when used in conjunction with PGNAA provide the complete analysis of hydrogen for comprehensive understanding of the CVD thin films.

5. SUMMARY AND CONCLUSIONS

NAA plays a complementary role in materials analysis in an industrial analytical laboratory. There are applications where it is highly desirable, and may play the dominant role as the method of choice e.g. bulk analysis of Si. The advantages of NAA are still the minimum sample preparation, and ultra high sensitivity while turnaround time, and lack of spatial resolution is a significant limitations.

The continued use of NAA in industries critically depend on having NAA trained professionals in the industrial organizations. It has been used most widely and innovatively when a NAA professional was part of the materials analysis laboratory. Interaction of the NAA professional at the research reactor with the industrial analytical laboratories is also very important for enhanced use of the technique. This is not quite as effective as having someone inside the industrial analytical laboratory however. Therefore training of young professionals in NAA, and other nuclear analytical methods is a key for the increasing use of the research reactors for materials analysis needs.