

More Than One Ever Wanted To Know About X-ray Detectors The First in a Series

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Spiderman carefully slid the sample of mud into the microscope. As he increased the magnification he caught sight of a tiny spherical crystal. Zooming in on it, he said "Let's see what it's made of". He reached over and flipped on the x-ray detector. As the spectrum formed on the screen a gasp went through the small group of researchers: "Kryptonite... the intruder is from another comic strip!"

The primary function of a microscope is to get a closer look at a sample. Many times a closer look is enough. Other times you need as much information as possible to solve a problem. In the above example, a reading of the chemical elements contained in the sample gave important clues about the sample's origin. X-ray analysis in electron microscopy combines elemental analysis with high resolution imaging. Of all the analytical techniques available to microscopists, it is the most highly developed and easiest to use.

An electron microscope uses an electron beam to form an image of an object. As the image is formed, the electron beam interacts strongly with the sample, creating (along with heat, light, and sound) x-rays. The electron beam gives an image of the sample. The x-rays contain information about the composition of the sample. Adding an x-ray spectrometer to an electron microscope can form a very powerful instrument.

When the electron beam strikes the sample it can generate x-rays in several ways. As the electrons strike the sample many are slowed, stopped, or deflected. The resulting change of momentum produces a broadband x-ray spectrum called continuous radiation or bremsstrahlung. As the incoming electrons disturb the inner shell electrons in the sample, the atoms

produce characteristic radiation in the form of x-ray spectral lines, just as the outer shell electrons produce light spectra and as vibrating molecules produce infrared spectra. Most of the x-rays produced in an electron microscope come from these two mechanisms.

The x-ray spectrum can be measured in two different ways. The most common directly measures the energy of each x-ray and is termed energy dispersive spectrometry (EDS). The other method measures the wavelength of the x-rays and is termed wavelength dispersive spectrometry (WDS). In the future I plan to discuss WDS in detail, but for now I will stick to EDS, since it is the most common.

Energy dispersive spectroscopy is like measuring the speed of a baseball by putting a thermometer in the catcher's mitt. An energy dispersive spectrometer measures the energy of each x-ray by letting the x-ray dissipate all its energy in a semiconductor crystal. Most of the energy is converted to phonons, but a predictable fraction of the energy goes to create free charges in the form of electron hole pairs. As these charges move through an electric field applied to the crystal a transient current flows, stopping when the charges either reach the electrodes or are trapped by crystal defects. The integrated current (or charge) from this event is proportional to the energy of the x-ray.

Making this measurement is literally a heroic effort. A magnesium $K\alpha$ x-ray will produce about 300 electron hole pairs. A boron $K\alpha$ X-ray will produce only 50 electron hole pairs. Current state of the art is to have a mean error in this measurement of 3 electrons. Literally hundreds of thousands of hours have been spent developing more efficient crystals, lower noise electronics, and optimized pulse processing to reach this level. If you have a Si(Li) detector system, you are in the presence of one of the lowest noise preamplifiers ever built.

Any semiconductor could be used as the detection crystal. The practical ones (in 1994) are silicon, germanium, mercuric iodide, and cadmium telluride. Of these only silicon and germanium are used in electron microscope spectrometers. Because of their relatively small band gaps, silicon and germanium must be cooled to liquid nitrogen temperatures to eliminate thermally generated dark current.

Silicon EDS detectors are used most of the time. It has so far proven impossible to purify silicon to the point that it has high resistivity at 77°K . This is primarily due to the presence of low levels of boron, which produces holes that carry leakage current. If you could match up a small atom willing to donate an electron with each boron atom you could "compensate" the crystal to have no net carriers at low temperatures.

This is what is done in a lithium drifted silicon (or Si(Li)) detector. Lithium is the only monovalent atom small enough to diffuse into silicon at low temperatures. If the diffusion is done in an electric field the lithium atoms (which are ionized at the drifting temperature) will drift into the crystal to form an opposing field. When the field in the crystal is canceled by the drifted lithium ions, the lithium stops drifting and the crystal is exactly compensated. After the drifting is completed the crystal must be kept cold to prevent the lithium from drifting out of it.

Germanium can be purified to intrinsic levels and does not need to be lithium drifted. Since germanium has a smaller band gap than silicon, an x-ray will generate more charges in a germanium crystal than a silicon crystal. This gives the germanium slightly better resolution. There are many technical problems with the production of germanium x-ray detectors. They have only recently been introduced into the marketplace.

EDS can detect all elements heavier than lithium. As the elements increase in atomic number the energies of their x-rays increase. The very light elements (beryllium through fluoride) require special detector ultrathin windows for detection. Elements heavier than sodium can be detected with standard beryllium window detectors.

P.S.: Kryptonite can be detected only under very special conditions. ■

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This article is intended as an overview of the field of x-ray spectroscopy and is the first of a series. Future articles will go deeper into this powerful technique. Comments, suggestions, etc. on the series are invited: Mark Lund, MOXTEK, INC. Tel.: (801)225-0930, Fax: (801)221-1121.

More Than One Ever Wanted To Know About X-ray Detectors

Part 2 - Settling the question of detector warming
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A combination of electron microscope and x-ray spectrometer is a very powerful tool. Not only can one see a sample in great detail, but one can determine, and even map, the chemical elements. In Part 1, I discussed some of the basics of energy dispersive x-ray spectroscopy (EDS or EDX). The heart of the spectrometer is a small piece of single crystal silicon about the size and shape of a shirt button, and about twice as thick. It has been selected for high purity, and then lithium drifted to compensate the remaining impurities.

The lithium is carefully drifted into the crystal button in order to exactly compensate the impurities in the crystal that would create leakage current. This is done at about 60° C under an electric field. It is then evaluated and re-drifted for a final clean up of any uncompensated impurity atoms that remain. These processes are very sensitive and the exact details are trade secrets in every case. After the lithium drifting is finished the crystal is fabricated into a detector by applying electrodes and passivating its surfaces. The finished detector is then installed in its Dewar, cooled to liquid nitrogen temperature and tested for final performance.

The finished detector is then kept at that cooled temperature for the rest of its useful life. Allowing the detector to warm up will allow the lithium to drift and ruin the detector. . . .

... Actually, the last sentence is not completely true. Certainly in the early years of Si(Li) detectors the wise ones kept them cold. Warming the detector not only encouraged the lithium to drift, but also cracked the passivation on the detector surfaces. However, this was not what the customer wanted to buy, and airlines complained about transporting this bomb-shaped object with white smoke pouring out of it. As the technology improved, it became possible to make detectors out of increasingly better silicon, which requires much less lithium. Passivation techniques were also developed which increased the stability of the detectors. A modern detector can be warmed and cooled hundreds of times without deteriorating. . . .

... Actually, the last sentence is not completely true either. While it is true that modern Si(Li) detectors will not be damaged by warming and cooling, there are other issues to be considered.

The spectrometer is constructed from a number of different materials including silicon, copper, aluminum, boron nitride, gold, Kovar, etc. - each with a different thermal coefficient of expansion. The heating and cooling of the spectrometer, over a range of some 220° C, will inevitably cause some "creaks" and "groans." These may have the effect of moving the contacts, and inducing scratches which may cause the detector surfaces to produce more noise. Thermal cycling will also stress other parts of the detector package. So...if you have an old detector DON'T WARM IT UP! If you have a modern detector you may warm it up occasionally without fear - - - but DON'T DO IT A LOT! And that is the truth (or at least good advice)!

Next I would like to talk about one of my heroes: Dr. U. Fano. Many people think that "fano" is another word for "fudge." as in fudge factor and others actually blame Dr. Fano for limiting detector resolution. He was, however, a pioneer in understanding the absorption of ionizing radiation. His influence in the EDX world is in the mathematical factor "F." While he did not name the factor, perhaps out of modesty, he did give it his initial. Others later took the hint and called it the Fano factor.

An energy dispersive detector works by absorbing an x-ray into the silicon crystal, and measuring the charge created in the crystal by the x-ray. This works best if all x-rays of a certain energy produce exactly the same number of electron-hole pairs in the detector. If they don't, there will be some broadening of the x-ray peak, giving a fundamental limit to detector resolution. You have already guessed that they don't, there is broadening, and there is a fundamental limit. These fluctuations are due to the quantum nature of the charge creation process. To understand how Dr. Fano comes in, we will go into a brief (and hopefully entertaining) discussion of statistics.

Say that you are camping in Yosemite and notice that every time you slap your knee you kill a hand full of mosquitos. By doing a controlled experiment you notice that by slapping four times a minute you kill on the average 100 mosquitos per slap. But you won't kill 100 mosquitos every slap, because the mosquitos don't fly in packs of 100, they just show up one at a time at random. Because the mosquito arrivals are independent you will find that the standard deviation in knee-kill-counts is the square root of the average number killed, i.e. 10. After a couple of hours, if you plot a histogram of the data, you will find a peak of 100 and a full width at half max. at $2.4 \cdot 10$, or 24 (2.4 converts standard deviation to full width half max.). Such independent processes are called Poisson statistics, which for reasonably large counts are approximated by Gaussian statistics.

Luckily for us, the generation of charge in a Si(Li) detector does not obey Poisson statistics. If it did, the statistical limit for resolution at FE-55 (Mn $K\alpha$) would be 350 eV, which is well over twice what the best Si(Li)'s actually achieve. The reason that charge creation in Si(Li) detectors does not follow Poisson statistics is that the generation of electron-hole pairs by an x-ray is not a series of independent events. This was discovered during World War II and was published by Dr. Fano in 1946 and 1947.

The difference between Poisson statistics and Fano statistics is just a constant (actually the square root of a constant), called the Fano factor (F). The Fano factor cannot yet be accurately calculated from theoretical considerations and it is very hard to measure. The best measurements have shown that the Fano factor for silicon is no larger than about 0.08. Thus the statistical limit of resolution is 3.5 times better than we would get without Fano (remember that F is under the square root).

So, the next time you hear a sales person say "our resolution is limited primarily by the Fano factor" you can tell him that his resolution is limited by quantum statistics, and that the Fano factor is increasing his resolution, saving his bacon, and feeding his children. Or you can just keep quietly smug.

All right, if the fundamental limit of resolution is 100 eV, why are the best Si(Li) detectors at around 130 eV? The reason is that other factors influence resolution including noise from leakage current, surface noise, incomplete charge collection, and preamplifier noise. I will discuss some of these fascinating topics in this column in the future.

A crystal with a lower band gap than silicon (i.e. germanium) will produce more charge than silicon. This will produce less statistical noise, which is the reason that the new germanium detectors have better resolution than with silicon. I will also discuss germanium detectors in this column in the future. ■

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More Than One Ever Wanted To Know About X-Ray Detectors

Part 3: Who Put Promethium In My Soup?

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The combination of electron microscope and x-ray spectrometer is a very powerful tool. Not only can one see a sample in great detail, but one can determine, and even map, the chemical elements. In Part 1, I discussed some of the basics of energy dispersive x-ray spectroscopy (EDS, EDX). In Part 2, I went into detail about the construction of the detector, and discussed counting statistics. In this installment I will discuss the interaction between the x-ray and the detecting crystal, things that can go wrong in the process, and the phenomena which can make false peaks in a spectrum.

An energy dispersive detector measures the energy of an x-ray by absorbing it, then measuring the energy absorbed. In Si(Li) detectors the x-ray is absorbed in a silicon crystal. The x-ray's energy is split several ways. Most of the energy goes to produce phonons. Phonons are just crystal lattice vibrations, which can be thought of as sound or as heat. The remainder of the energy goes to produce free charge-electrons which are removed from their home atoms with enough energy to move freely through the lattice. These leave vacancies at home, which also can be seen to move freely through the crystal, hopping from one atom to the next. These are what is termed as "holes," and act just like positively charged electrons. Under the influence of an external electric field these electrons and holes will move in opposite directions, causing current to flow in the detector electrodes until they hit the electrode, where they are absorbed back into the lattice. The amount of charge that flows in the external circuit during this time is the signal, and is proportional to the energy of the absorbed x-ray.

One thing that can go wrong with this process is that the absorbed x-ray might excite a silicon atom in the detector to emit a silicon x-ray. If this x-ray is then re-absorbed in the crystal there is no problem, but if the new silicon x-ray escapes from the crystal without being absorbed it leaves an energy deficit equal to the energy of the silicon k line. These events will cause a separate peak to form 1.74 keV below the real peak. This is called an "escape peak." Only x-rays that have higher energy than 1.84 keV (the silicon absorption edge) can produce escape peaks, and because escapes are rare they are usually only seen when a strong peak is present. Their height is typically less than one percent of their parent peak.

Another thing that can go wrong is overlap. EDX detectors can only

detect one x-ray at a time. This includes not only signal x-rays, but background x-rays and stray electrons from the microscope beam. If two x-rays come in at exactly the same time they will look like a single x-ray to the detector. The energy the detector will report to the computer will be the sum of the two energies. This causes artifacts known as "sum peaks."

If two x-rays come in together, but not exactly at the same time, the second x-ray generates a new pulse of charge before the previous one has been fully collected. This gives the same effect as the scale at the doctor's office—when you step on it the nurse always puts her foot on it (which is why you always weigh more at the doctor's). If uncorrected this will give a high energy tail to the peak. This type of coincidence can be detected by the electronics, which will reject both x-rays. The circuit that does this is called the "pile-up rejector."

Another artifact that can be seen with Si(Li) detectors is a small silicon peak. This probably comes from fluorescence of silicon in parts of the detector that are outside the active region—the flange or the thin dead layer at the surface.

Interferences are lines from two elements that the spectrometer cannot resolve. This can take two forms. An example of the first is calcium versus potassium. These are neighboring elements which the spectrometer can easily resolve if they are in similar concentrations. In biological analysis, however, there are often high concentrations of potassium and low amounts of calcium. The huge potassium peak has a tail that overlaps the calcium, making it difficult to detect.

The second form of interference is due to L or M lines of heavy elements interfering with K lines of light elements. An example of this is the interference of the vanadium $L\alpha$ and $L\beta$ and the oxygen $K\alpha$.

Artifact lines from these phenomena show up in the spectrum, and so a search for possible elements will often show unexpected elements. Usually these matches come from the heavy elements. Since they each have many lines there is a good chance one will match your artifact. It can be quite a surprise to find promethium or francium in your sample. If it is a surprise, check for artifacts. A good way to do this is to look for other lines for the same element. For example, if the promethium $L\alpha$ line at 5.432 is found, look for the $L\beta$ line at 5.960 keV, or the M lines. Usually you will find that the surprises are artifacts, and that your sample is actually quite boring! ■

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More Than One Ever Wanted To Know About X-ray Detectors Part IV: Windows for Elements Heavy and Light

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I attend a local entrepreneur's luncheon once a month. Since the small town I live in is the home of Word Perfect Corporation, and Novell, Inc. is just down the road, you can imagine that many members are doing exciting things with software. When I tell them that MOXTEK makes windows for X-ray detectors they really light up, until I tell them that I mean *real* windows.

X-ray detectors are used in electron microscopy to add chemical element analysis to the imaging capability of the microscope. A typical energy dispersive spectrometer uses a silicon crystal about the size of a shirt button to detect and measure the energy of incoming X-rays. This crystal is cooled to 77 degrees Kelvin, or to the temperature of liquid nitrogen. This cooling lowers the noise and stabilizes the detector. It also makes the detector vulnerable to vapors condensing on its surface. X-ray windows solve this problem by isolating the detector from the environment.

Anything that you put between your sample and the detector is likely to disturb, degrade, and generally make a mess of your precious signal. X-ray windows are no exception. The various window options do this in different ways.

There are several options for X-ray windows used in electron microscopes. These are beryllium, boron nitride, boron hydride, diamond, and polymer. The oldest of these is beryllium. Beryllium is most useful for detecting elements heavier than magnesium. It is possible to use the thinnest beryllium foils (5 μm) for sodium and fluorine. For the light elements (boron, carbon, nitrogen, oxygen, fluorine and sodium) special windows have been developed. These go by the generic name of ultrathin windows. Of the several technologies used to make ultrathin windows, they all have a few things in common. The X-ray transparent membranes are very thin, about 50 $\mu\text{g}/\text{cm}^2$. This is only a couple of thousand atoms thick. The membrane materials are all remarkably strong and they are made from materials containing only light elements. The membranes are supported on grids to provide strength over large areas.

Boron nitride windows were the first light element windows. They are made with a chemical vapor deposition (CVD) process with the grid a monolithic part of the structure. Diamond windows (which are no longer commer-

cially available) and boron windows (which are also available with CVD, but on a silicon grid. Polymer windows are made of ultrathin superpolymer membranes stretched across a silicon, boron nitride, or tungsten grid. All of these windows are usually coated with a 200 to 800 \AA thick layer of aluminum to cut down light transmitted through them and to make them electrically conductive. In addition, a coating of aluminum or aluminum plus aluminum nitride is necessary to stop gas diffusion through the polymer windows.

The transmission of ultrathin windows depends greatly on the window material and the X-ray energy. Windows containing boron, for example, will transmit boron X-rays very well, since the $K\alpha$ emission energy is slightly lower than the boron absorption edge. The boron will strongly absorb carbon X-rays, however. Likewise, diamond windows are very good for carbon and boron X-rays, but poor for nitrogen. Multielement windows such as boron nitride, boron hydride, and polymers have better transmission at absorption edges than pure element windows.

Reliability of ultrathin windows is surprisingly good, considering how thin they are - the transmissive area is about 50 $\mu\text{g}/\text{cm}^2$. Ultrathin means ultrafragile. You cannot touch an ultrathin window with your finger, bump it with a stage, or clean it with a cotton swab. However, ultrathin windows can be quite reliable. Reliability data is proprietary, so I can only report on MOXTEK results. One spectrometer manufacturer who uses MOXTEK windows has over 1000 ultrathin window systems in the field and an accumulated mean time before failure of 484 weeks as of April 1995 and going up. That is over nine years. When fitting a new thin window system on an old microscope, it would be good to discuss window reliability with both the microscope and EDS manufacturer.

In certain applications, however, reliability can be poor. The biggest problem is particle impact on the window during microscope venting. This causes "bullet holes" in ultrathin windows and depends on the gas dynamics inside the microscope. Many electron microscopes do not have this problem, but some models have a high propensity for window damage. Environmental SEMs, which can expose the window to reactive gases and hot water vapor, are particularly hard on ultrathin windows. The aluminum on polymer windows tend to become etched, which allows water permeation. To solve this problem, MOXTEK has developed a boron membrane window that is immune to attack from corrosive gasses.

Cleaning X-ray windows is a tricky proposition. Even beryllium windows are used near the limit of their strength in order to give good X-ray transmission. If it is clear that the window is contaminated (vacuum oil dripping off the mount is a good sign of this) call the manufacturer for advice on how to clean it. If you do not mind voiding the warranty, an effective, and not-too-dangerous, method of cleaning is to gently run a stream of alcohol across the surface. Do not squirt the window membrane directly. Contact the EDS manufacturer for more details! ■

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More Than One Ever Wanted To Know About X-ray Detectors Part V: Wavelength - The "Other" Spectroscopy

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The use of x-ray spectrometry in electron microscopy has been a powerful market driver not only for electron microscopes but also for x-ray spectrometers. More x-ray spectrometers are sold with electron microscopes than in any other configuration. A general name for the combination is AEM, or analytical electron microscope, though in modern times AEM can include other instrumentation such as electron energy loss spectroscopy and visible light spectroscopy. In previous articles I have discussed energy dispersive spectrometers (EDS). These use semiconductor crystals to detect the x-rays and measure the energy deposited in the crystal. A second type of x-ray spectrometer measures the wavelength of the x-rays, and so is called "wavelength dispersive spectrometry" (WDS).

Wavelength spectrometers use crystals to diffract x-rays similar to the diffraction of visible light by gratings. The regularly spaced array of atoms (or molecules) in the crystal diffract x-rays. Unlike diffraction gratings, however, the crystal reflection only reflects one wavelength for each angle of incidence. This is due to the difference between the two-dimensional diffraction of a grating and the three dimensional diffraction of a crystal lattice. Diffraction from a three dimensional structure is called Bragg diffraction. In Bragg diffraction the angle of reflection is equal to the angle of incidence just as if the crystal were a mirror. Only one wavelength and its shorter wavelength harmonics can be reflected for a given lattice spacing and angle of incidence. This means that most crystal spectrometers must either be scanned or remain at one fixed wavelength. The exception to this statement is a small class of spectrometers that use a geometry that allows the x-rays to simultaneously

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intersect the crystal at a range of angles, a different angle for each segment of the crystal. These have very small collection solid angles and require a position sensitive detector to record the spectrum.

A crystal can only diffract x-rays that are shorter in wavelength than twice the distance between the atoms (or molecules). This means that there is not one crystal that will work for the whole x-ray range. Short wavelength x-rays can use crystals of typically 1 to 5 angstrom spacings. X-rays from the lighter elements need crystals with wider spacings, which are typically organic crystals with large molecules. These crystals exist at spacings shorter than about 13 angstroms and cannot be used for elements lighter than fluorine.

For the lightest elements artificial crystals are used, either Langmuir-Blodgett films or, more recently, sputtered multilayers. Langmuir-Blodgett films are made from soaps that contain heavy metals. The soap molecules can be floated on water with their hydrophilic ends in the water and their hydrophobic ends up, giving a uniform layer one molecular layer thick. When a substrate is repeatedly dipped into the water, the soap layer is picked up onto the surface one layer at a time, making an artificial crystal with the molecules aligned within each layer. The layer stack can then be used to diffract x-rays. Sputtered multilayers are made by physical vapor deposition, with alternating layers of heavy and light elements. These multilayers can be made at custom spacings from about 15 angstroms to 200 angstroms or more. They have higher reflectivities than the soap films and are more stable.

The first x-ray spectrometer-electron microscope combinations were special purpose WDS instruments. The microscope was specifically modified to have a spectrometer bigger than the column on which it was built. The combinations were useful as prototypes of analytical microscopes and were used to develop AEM techniques, but it was not until EDS was developed that analytical electron microscopes became popular.

Today there are many applications of WDS, and several companies make WDS spectrometers for use with both TEMs and SEMs. The advantages of WDS are higher resolution and lower background. Typical resolution of a WDS spectrometer is 20 eV (at Mn $K\alpha$), whereas the best EDS spectrometers have 130 eV. At Na $K\alpha$ the WDS can give as low as 3 eV FWHM versus 80 eV for EDS. These advantages give WDS the edge in measurements where minimum detectable limits are important. They also make possible measurements such as potassium in a high background of calcium, which is important in some areas of medicine and biology. The disadvantage of WDS is low throughput. WDS spectrometers collect a relatively small solid angle and must be slowly scanned to obtain a spectrum. A recent commercial development is the integration of both WDS and EDS in one unit with the hardware and software to collect, analyze and display their spectra simultaneously.

WDS spectrometers use an angle scan to generate a spectrum. The crystal moves and rotates and the detector moves along at twice the speed to keep up with the mirror reflection, giving what is called a theta-two-theta scan. This takes a lot of space and precision mechanics. Since collimating optics are not available in the x-ray region, the crystals are efficient only over a small solid angle and collection efficiency is low. Detectors are typically flow proportional counters, which have a high count rate capability and sensitivity to even the softest x-rays.

X-ray spectrometry is a good example for pondering nature's constraints. EDS does not have to be scanned, and so can detect an entire spectrum at once. On the other hand, an EDS spectrometer can only detect one x-ray photon at a time and does not care whether the x-ray is in your range of interest or not. This could cause your maximum count rate to be exceeded by spectra outside your range of interest. WDS spectrometers can withstand very high background or signal count rates, but can measure only one wavelength at a time. Simultaneous WDS spectrometers always give up either collection area, or spectral range in order to give a simultaneous spectrum. These constraints are not easily resolved, and so the best spectrometer depends on the exact application. This leaves room for both EDS and WDS in modern analytical electron microscopes. ■

More than One Ever Wanted to Know about X-Ray Detectors Part VI: Alternate Semiconductors for Detectors

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X-ray spectrometers give the capability to determine chemical element composition in electron microscopes. The semiconductor with the most experience as an x-ray detector is silicon. Silicon is the most highly developed material on earth, and has a lot of good things going for it, but for some applications we crave something with other good properties. For example, for room temperature detectors it would be best to have a semiconductor with a wider band gap. For higher resolution it would be better to have a semiconductor with a smaller band gap. For these reasons a number of other semiconductors have been developed as x-ray detectors. In this article I will talk about narrow band gap semiconductors. Next time I will discuss large band gap semiconductors.

As I discussed in Part II, the resolution of energy dispersive detectors is limited by the Poisson-Fano statistics of the charge generation process. The more charge generated by an x-ray the smaller the noise from this source. Thus one of the trends in EDX is to move to semiconductors with smaller band gaps. The natural place to go from silicon is germanium, which has 1.3 times the charge generation. The Fano factor of germanium also seems to be about 20% lower than silicon. These two factors give germanium about a 25% resolution advantage over silicon without considering the electronic noise, which will dominate at low energies.

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Germanium was used as an EDX detector from the very beginning of EDX and has always been the preferred material for gamma ray detection. Due to technical problems it has not shined as an x-ray detector material until recently. It has several advantages besides the noise. In the "old days" germanium was lithium drifted to make Ge(Li) detectors. In the modern age germanium can be made purer than silicon, and so does not have to be lithium drifted. It has much higher stopping power than silicon. It has higher mobility (and mobility-lifetime product) which allows the charge to be collected more completely. Germanium detectors have been used extensively in gamma ray spectroscopy due to this ability to collect charge over large volumes and their high stopping power. High resolution germanium x-ray detectors have only been available very recently due to some problems that germanium presents.

Germanium has also had its drawbacks. One of the worst is a by-product of its high stopping power. At Al $K\alpha$ 25% of the x-rays are stopped within the first 0.1 micron. This means that the detector "dead layer" must be very small or partially collected charge will widen the x-ray peaks. The electric fields must also be high to prevent part of the charge from diffusing to the top surface of the detector where they will recombine. Germanium is sensitive to infrared light, and so requires a separate cooled window in the cryostat to block this light.

As I discussed in Part III, a common artifact in EDS is the escape peak, which happens when a signal x ray loses some of its energy by creating a fluorescent x-ray in the detector. Most of these secondary x rays will be reabsorbed by the detector. However, some of the secondary x-rays escape from the detector, leaving a deficit in the signal and producing a ghost peak. Silicon has an absorption edge at 1.84 keV, and its escape peaks are 1.74 keV below each parent peak. Germanium has no escape peaks up to its absorption edge at 11.1 keV. (There is a theoretical possibility of an escape peak from the Ge $L\alpha$, but this peak has not been seen.) This is great if there are no x-rays coming into the detector with energy greater than 11.1 keV. If there are then you get an unexpected bonus of two escape peaks 1.1 keV apart, one from the Ge $K\alpha$ and one from the Ge $K\beta$. In a complicated spectrum this could be quite a mess: for zirconium the escape peaks from both Zr $K\alpha$ and Zr $K\beta$ are all resolved. In addition the higher fluorescence yield of germanium makes the ratio of escape count to $K\alpha$ ten to a hundred times higher than silicon. This is why computers were invented!

If germanium, with its smaller band gap, can give better resolution how about other small-band-gap semiconductors? HgCdTe has an adjustable band gap clear down to zero, as do some other ternary (three-element) compounds. Theoretically these materials could be used to give much better resolution. These narrow band gap semiconductors have been developed for infrared detectors and are very successful. However, they have a lot of leakage current due to the difficulty in preparing ultra-high quality crystals from ternary compounds. Infrared detector systems have tons of signal which can easily make up for the leakage current, but x-ray detectors must detect pulses of only a few dozen electrons. There is always hope that narrow-band-gap semiconductors will improve in quality to the point that they can be used.

I wonder how many researchers have wished, as I often do, to travel back in time to the Creation of the Universe and make a simple request. My dream is to have three more chemical elements in column IVA in the periodic table--one inserted between diamond and silicon, one between silicon and germanium, and one between germanium and tin. Having these elements would give the x-ray detector business a big boost! I would gladly give up erbium, thulium and ytterbium for silicon-plus, germanium-plus, and tin-plus! Why? As you go down column IVA the bandgap decreases from diamond (5.5 eV) to tin (exactly zero). Single element crystals are much easier to make perfect than are compounds. An intermediate between germanium and tin would have a narrow band gap, high stopping power, and excellent crystal perfection, and would make a great detector. There are similar good reasons for making detectors from silicon-plus or germanium-plus.

One approach to this (without a time machine) is to make compounds or alloys of the column IVA elements. In most cases a compound or alloy of two semiconductors will have a band gap intermediate between the two constituents. If we could just lift the band gap of tin a couple of millielectron volts... Unfortunately tin does not make compounds or alloys with carbon, silicon or germanium. This leaves us without a column IVA (i.e. covalently bonded) possibility for a band gap lower than germanium. Likewise carbon and germanium are incompatible, but such combinations as silicon carbide or silicon-germanium alloys have interesting properties that I will discuss in the next article. ■

More than One Ever Wanted to Know about X-Ray Detectors Part VII: More Alternate Semiconductors for Detectors

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Where did the term "Energy Dispersive Spectroscopy" come from? In the beginning (that would be about 1965) there was only "x-ray spectroscopy," which meant "wavelength dispersive x-ray spectroscopy." When semiconductor detectors came on the scene there was a possibility of confusion, so the new method had to have a new name. Very soon there were a variety of names, including "nondispersive spectroscopy," "energy analyzer," "pulse height spectroscopy," "semiconductor counter spectroscopy," and "semiconductor x-ray spectroscopy," as well as "Si(Li) [and Ge(Li)] spectrometers." Of course no one was going to try to raise money to manufacture "Si(Li) spectrometers"; they would be laughed at! (This business is only slightly silly.)

About 1972 the term "energy dispersive spectroscopy" was gaining prevalence, and people had started to rename the Bragg reflection spectrometers "wavelength dispersive." There was some resistance because the Si(Li)-based spectrometer does not disperse, it just detects. Semiconductor detectors are energy-sensitive spectrometers. Likewise, Bragg spectrometers do not "disperse" in the same way that a prism or grating disperses visible light, since only one wavelength is reflected at a time. You could say that a shotgun disperses shot, but not a rifle; a crowd could disperse, but not an individual. Bragg spectrometers are "wavelength sensitive" spectrometers. How-

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ever, the purists lost the battle, and the slightly cockeyed definitions took over. Last month I discussed small band gap semiconductors and their potential advantages. There are also semiconductors with larger band gaps than silicon and germanium, and a lot of research is being put into them. Wide band gap semiconductors include diamond, silicon carbide, cadmium telluride, gallium arsenide, mercuric iodide, and lead iodide.

The biggest advantage that a wide band gap semiconductor could give to x-ray detection is operation at room temperature. At room temperature even the highest resistance silicon and germanium have leakage current due to thermal ionization of carriers. The forbidden band gap is small enough that some room-temperature electrons can jump it. So silicon and germanium must be cooled to liquid nitrogen temperatures to prevent this. As the band gap gets larger the probability that an electron will jump it becomes less and less, until at band gaps of a couple of electron volts there is no thermal leakage current at room temperature.

As I discussed last month, a large band gap detector will produce less charge when it absorbs an x-ray. This gives more statistical noise and less resolution. On the other hand, a room temperature detector could be made smaller, lighter, cheaper, and more portable than a liquid nitrogen cooled detector. There are many applications in which high band gap detectors would work well.

The only single-chemical-element semiconductor with a wide band gap is diamond. The band gap of diamond is 5.5 electron volts. This is much higher than is needed for a room temperature detector, so the statistical noise is high. Diamond has great electron mobility, however, and successful radiation detectors have been made with it. Unfortunately, carbon is a light element and you need a lot of it to stop your typical x ray. The only diamonds that are perfect enough for x-ray detection are those that are perfectly colorless and transparent. Large, clear diamonds are in great demand for boring applications such as body adornment. Diamond x-ray detectors will probably not hit the market any time soon.

This leaves us with compound semiconductors, a number of which are available. The problem with compound semiconductors is that they are very hard to make perfect. Even though the band gap may be high enough for high resistivity at room temperature, lattice defects, impurities, and surface problems can also induce leakage current. A number of high band gap compound semiconductors have been studied, but most have had leakage current that prevented their use at room temperature. The two that have been useful are mercuric iodide (HgI_2) and lead iodide (PbI_2). These seem to have a mechanism to self-compensate defects and impurities, and so have high resistivity. Both HgI_2 and PbI_2 have been used to make good x-ray detectors and will soon make a splash in the marketplace.

In Part VI I mentioned that one way to get a desired band gap is to make an alloy or compound of two or more group IVA elements. For example, silicon and germanium form a continuous series of solid solutions, and the band gaps of their alloys are also continuous between those of the pure elements. Unfortunately a detector made of such an alloy would not have much advantage over one of pure silicon or pure germanium. It would have a lot of escape peaks, though!

An alloy of silicon and carbon would be nice, allowing flexibility to exactly define the trade off between operating temperature and resolution. Of course there are no alloys of silicon and carbon, only one compound--silicon carbide. Silicon carbide is hard to make in a big chunk because it has a high melting temperature and crystal phase transformations between the growth temperature and room temperature. Small wafers of SiC have been made by vapor transport, but they are too low in resistivity to make x-ray detectors.

In conclusion, silicon will continue to be used for most x ray detectors. Germanium is now being introduced as a high-performance option. HgI_2 will soon be introduced as a moderate resolution detector for low cost and portable applications. ■

More Than One Ever Wanted To Know About X-Ray Detectors Part VIII: If I Know It's There, Why Can't I See It?

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This month we are going to deviate from Mark Lund's normal discussion and talk about one of the practical problems that must be considered when using an x-ray detector on a scanning electron microscope to solve real-world problems.

Several years ago I worked in the analytical laboratory of a major semiconductor manufacturer. One day a process engineer came into the lab and asked us to develop an analytical method to determine the amount of copper in an aluminum film on a silicon wafer. The levels of copper would be somewhere between 0.5% and 1.0%. He gave me a sample, saying that he didn't know the exact concentration of copper but was certain that it was at least 0.5%.

Well, being smart analytical chemists we determined that we wanted to do as little sample preparation as possible to get the analysis (we were a little bit lazy, too, but who isn't?). We fractured the wafer and mounted a small piece for analysis using the EDS x-ray attachment on our SEM. We knew this wouldn't be a quantitative analysis, but just wanted to make sure there would be adequate signal for quantification later. Much to our chagrin there was almost no copper signal distinguishable above background in the x-ray spectrum that we collected. This was a particularly disconcerting result because we'd promised the engineer we'd have a method developed within the week, and now we were going to have to do some real work! Why couldn't we see the copper in the spectrum?

First you must understand that in order to say conclusively that there is a peak in the x-ray spectrum, the peak must be statistically "above background". X-ray events occur in a Poisson distribution, which was discussed by Mark in Part 2 of this series. The standard deviation of this distribution is the square root of the counts. In order to say with 98% certainty that a peak is real, the peak height must exceed the height of the background by $2(\text{background})^{1/2}$. If the x-ray counts in a peak exceed the background by $3(\text{background})^{1/2}$ there is nearly a 99.9% certainty that the peak exists. Since we couldn't see the peak conclusively we either had too much background or not enough peak, or both!

Let's look at the background side first. If there is no spectral overlap of characteristic lines and no artifacts in the spectrum, then the main contribution to the background near the x-ray peak is broadband bremsstrahlung. (I am told that bremsstrahlung is German for "braking radiation".) Bremsstrahlung radiation is produced whenever an electric charge changes speed or direction. As SEM beam electrons interact in the sample, they can approach near enough to the nucleus of a sample atom to be deflected by its positive charge. The resulting change in direction is an acceleration of the electron, and an x-ray photon is emitted. This process can occur numerous times until the electron loses all of its kinetic energy. Occasionally, an electron is brought to rest in a single collision, and its entire kinetic energy is converted into a single photon of equivalent energy. So the maximum energy of the broadband bremsstrahlung is equal to the accelerating potential of the SEM, and the shape of the background continuum is determined both by the accelerating voltage and by the sample material.

Unfortunately, since the production of bremsstrahlung is fundamental to the physics of the electron-matter interaction, there are very few remedies for reducing the background. One way to reduce the bremsstrahlung is to reduce the amount of matter for electrons interaction. Rather than placing the sample on a typical SEM stub, which is infinitely thick to electrons, the sample can be placed on a thin polymer film. If the polymer is sufficiently thin then many of the electrons will pass through without losing large amounts of kinetic energy to bremsstrahlung, significantly reducing the x-ray background. In our laboratory we are currently performing experiments to demonstrate the improvement in sensitivity using this technique and hope to publish our results during the next year.

Now that we've looked at background, what about the size of the peak? When an electron beam is incident on a sample it interacts not just at the surface but within an interaction volume. This volume is shaped somewhat like a pear -- narrow at the top and spherically shaped at the bottom. It turns out that the depth range of 20 KV electrons in silicon or aluminum is about 3 microns, with a similar lateral distance being excited. Since the thickness of the aluminum film we were investigating was less than 1 micron, the majority of the volume being analyzed was the silicon wafer rather than the aluminum film. This hurts us in two ways. First, rather than being 0.5% in concentration, the copper atoms are now maybe only 0.05% or less of the total atoms in the excitation volume. Second, we now have a significant number of silicon x-rays in the spectrum. Since the detector can only process one x-ray at a time, as we tie it up processing silicon x-rays it is not available to process copper x-rays.

There are at least three ways to get around these problems. Reducing the accelerating voltage on the SEM will reduce the penetration depth of the electrons and result in a smaller excitation volume. This increases the effective concentration of the copper. However, the accelerating potential must be kept above the K shell absorption edge in order to produce x-rays, and should normally be at least twice this energy. For copper the K shell absorption edge is 8.98 KeV, so we would want to be at 18 KV or above for the SEM accelerating potential. So this isn't a real good option for copper but is particularly effective for lighter elements.

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Part IX: Antigravity Holes

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In this series we have explained why x-ray spectrometers are useful in electron microscopes and, to some extent, how they work. In this article I will discuss some of the physics behind the detector.

First I have been asked to explain what a hole is. In a silicon crystal every silicon atom is bound to four others with covalent bonds. Every electron has a home, which consists of its home atom in the case of the inner electrons. The four outer (or valence) electrons have a home on the road, shuttling back and forth between two atoms each. In this way the five atoms share eight electrons among themselves.

When a phosphorus atom is put into the lattice it can participate in bonds with all the bonds of the silicon atom it replaced and have one extra electron that cannot participate in a covalent bond. This electron is easy to separate from the phosphorus atom and, after it does, it is free to roam around the crystal, but it leaves behind a fixed positive charge on the phosphorus atom's nucleus which cannot move. This extra positive charge is no longer cancelled by having the free electron close by. Likewise, a boron atom can fit into the lattice, but it lacks an electron to link up with all its silicon neighbors. It is easy for an electron from a nearby silicon atom's valence shell to flip over into this position which then makes the boron atom look as if it is charged negative. It also leaves the neighboring silicon atom without one of its electrons, which makes this atom look like a positive charge to the normally neutral lattice.

As other electrons move in to fill the gap one at a time, the electron vacancy moves in the opposite direction to the electrons. For most applications this vacancy can be considered to be a positive charge moving

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through the lattice. Because it is not a real particle, and the lack of a particle, it is called a hole. When a free electron from a phosphorus atom meets a hole from a boron atom, it can fill it. When it does this the electron and hole "disappear" into the lattice, because the electron takes up permanent residence in the last covalent bond that the hole appeared in and the lattice looks normal. The only evidence left is that their original boron and phosphorus "home" atoms are still charged. When boron and phosphorus dopants are uniformly scattered through the lattice the charges just cancel each other out. When they are in different parts of the crystal an electric field forms between them, which is what makes the built-in voltage of a p-n junction.

Now let's consider a pure silicon crystal with an electric field on it. When an x-ray is absorbed it knocks an electron out of its covalent bond, leaving a hole behind. Left on its own it would find its home again, or one just like it. When an electric field is applied to the crystal, however, it can't find its home and moves along with the field toward the positive electrode. Likewise, the hole gets filled with another covalent electron from one of the neighboring atoms trying to move with the field, and it appears as if the hole were moving toward the negative electrode. Semiconductor workers soon tire of remembering that it is the electrons that are moving and talk about the holes as if they were the actual charge carriers with mass, mobility, lifetimes, etc. This is OK because they act just like positive charges in the crystal. Just about the only thing you can't do with holes is shoot them out into space.

Notice the fundamental difference between the way that dopants form charge carriers and the way that x-rays form charge carriers. When an electron or hole leaves a dopant atom, it leaves a fixed charge behind because the nucleus of the atom can't move. When an x-ray generated electron-hole pair leave an atom, they leave a neutral atom behind and can both move in the electric field of the detector.

An interesting thing about holes is they have negative mass--they are antigravity. Do you remember driving with a helium balloon in the car? When you slam on the brakes the balloon flies to the back of the car, just the opposite direction of the children and soft drinks. (Don't get into a wreck trying this at home; get one of the kids to drive while you experiment in the back seat.). The apparent negative mass of the balloon is due to the fact that it is less dense than the air. When the air is rushing to the front of the car, it pushes the balloon back. In the same way, since the hole is an absence of an electron it should float to the top of the crystal. A simple way to build an antigravity machine is to shoot the holes out of the crystal onto the bottom of your chair! Of course the holes don't actually float to the top of the crystal because gravity is very weak compared to the other forces in the crystal and, as I mention before, you can't remove holes from the crystal.

When an x-ray hits the detector a charge is created proportional to the x-ray energy. Initially this does not affect the fields inside the detector because the cloud of positive and negative local charges overlap exactly, giving a net charge of zero. Soon, however, the electrons and holes start to separate due to the applied electric field. As the charges move they induce a current to flow on the detector electrodes. This current is the signal, which is then amplified and processed to form a point in the spectrum. ■