Table 8.7 Typical Primary Beam Filters and Range of Use in EDXRF Systems

Filter	Thickness (μm)	X-ray tube range (kV)	Elements	Comments
None		4–50	Na–Ca	Optimum for light elements, 4–8 kV excitation[a]
Cellulose		5–10	Si–Ti	Suppresses tube L lines (see Fig. 8.16.)[a]
Al, thin	25–75	8–12	S–V	Removes tube L lines[a]
Al, thick	75–200	10–20	Ca–Cu	Used for transition elements
Anode element, thin	25–75	25–40	Ca–Mo	Good for trace analysis[b]
Anode element, thick	100–150	40–50	Cu–Mo	Trace analysis with heavy element L lines[b]
Cu	200–500	50	>Fe	Suppresses tube K lines

Source: Table modified from Ellis, used with permission.

[a] He purge or vacuum path needed to avoid attenuation of low energy lines.

[b] Serves as a secondary fluorescence source, also called a monochromatizing filter; preferentially transmits tube K lines.

8.2.7.1. Semiconductor Detectors

When an X-ray falls on a semiconductor, it generates an electron ($-e$) and a hole ($+e$) in a fashion analogous to the formation of a primary ion pair in a proportional counter. Based on this phenomenon, semiconductor detectors have been developed and are now of prime importance in EDXRF and scanning electron microscopy. The principle is similar to that of the gas ionization detector as used in a proportional counter, except that the materials used are in the solid-state. The total ionization caused by an X-ray photon striking the detector is proportional to the energy of the incident photon.

The most common semiconductor detector for laboratory EDXRF systems is the *lithium-drifted silicon diode*, represented as Si(Li). (It is called a "silly" detector for short). A schematic diagram of a silicon lithium-drifted detector is shown in Fig. 8.30. A cylindrical piece of pure, single crystal silicon is used. The size of this piece is 4–19 mm in diameter and 3–5 mm thick. The density of free electrons in the silicon is very low, constituting a p-type semiconductor. If the density of free electrons is high in a semiconductor, then we have an n-type semiconductor. Semiconductor diode detectors always operate with a combination of these two types.

The diode is made by plating lithium onto one end of the silicon. The lithium is drifted into, that is diffused into, the silicon crystal by an applied voltage. The high concentration of Li at the one end creates an n-type region. In the diffusion process, all electron acceptors are neutralized in the bulk of the crystal, which becomes highly nonconducting. This is the "*intrinsic*" material. The lithium drifting is stopped before reaching the other end of the silicon crystal, leaving a region of pure Si (p-type), as shown in Fig. 8.30. Submicron gold layers are applied at each end as electrical contacts. The detector is reverse-biased, removing any free charge carriers from the intrinsic region. Under this condition no current should flow since there are no charge carriers in the intrinsic region. However, the band-gap between the valence band and the conduction band is small, only 1.1 eV for Si(Li). At room temperature, thermally generated charge carriers cross this barrier easily and become conductive even with no X-ray photons striking the detector. This causes a high noise level. To decrease this noise
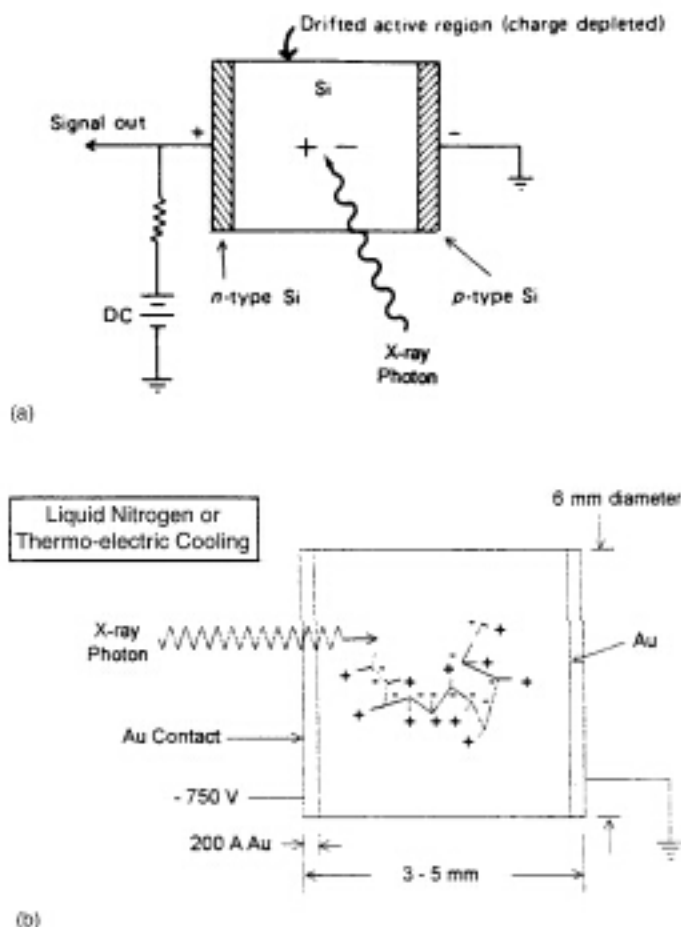
(a)

(b)

Figure 8.30 The Si(Li) semiconductor detector. (a) Schematic shows the n-type Si region on one end of the Si crystal, a central charge depleted intrinsic region and p-type Si on the other end. (b) The actual detector has 200 Å layers of gold as electric contacts on each end of the crystal. An X-ray photon striking the intrinsic region generates electron–hole pairs within the diode. [Fig. 8.30(b) courtesy of Thermo ARL (www.thermoARL.com).]

and increase the sensitivity of the detector, the temperature of the system must be decreased significantly. This is accomplished by cooling the detector to 77 K with liquid nitrogen, which must be replenished regularly. In exactly the same fashion, germanium, also in group IV of the periodic table, can be used instead of silicon, making a Ge(Li) drifted detector (you might guess this is called a "jelly" detector). The Ge(Li) detector also requires liquid nitrogen cooling, since its band gap is only 0.66 eV.

An X-ray photon striking the detector produces multiple electron–hole pairs in the intrinsic region [Fig. 8.30(b)]. The number of electron–hole pairs produced is proportional to the photon energy. The energy required to make an electron–hole pair is 3.86 eV in Si(Li), so the number of electron–hole pairs formed is approximately

$$n = \frac{E}{\varepsilon} = \frac{E}{3.65\,\text{eV}} \tag{8.17}$$

where n is the number of electron–hole pairs; E, the energy of the incident X-ray photon (in eV); and ε, the energy to form an electron–hole pair in eV.

For a similar Ge lithium-drifted detector, the energy required for ionization is 2.96 eV. This is much less than the energy required for ionization in a proportional counter or a NaI(Tl) scintillation detector.

Under the influence of an applied voltage, the electrons move toward the positive end and the holes toward the negative end of the detector. The total charge collected at the positive contact is:

$$Q = nq_e \tag{8.18}$$

where Q is the total charge in coulombs (C); n, the number of electron–hole pairs = E/ε; and q_e, the charge on one electron = 1.69×10^{-19} C/electron.

The collection of charge results in a voltage pulse. Since the total charge is proportional to the energy of the incident photon, the amplitude of the voltage pulse produced is also directly proportional to the energy of the incident photon. The voltage pulses are amplified and "shaped" electronically and sent to a *multichannel pulse height analyzer* to be sorted by pulse height and counted.

The operation of a multichannel analyzer can be modeled in a simple fashion. Assume that we have a pulse height analyzer of a given total voltage range with the ability to change the voltage in small increments. As an example, the total voltage range is 10 V and the interval of change is 0.1 V. X-rays of short wavelengths (high energies) must be separated from X-rays of long wavelengths (low energies). That is what a pulse height analyzer does; it rejects energy signals that are higher or lower than a selected energy window. If the analyzer window can be changed in small energy increments, only photons with that energy will pass through. Those photons are counted and stored in that energy window location in the analyzer memory. Each energy window location is called a *channel*. Then the energy window (voltage) is changed by 0.1 V and only photons corresponding to the new energy window will pass through and be counted and stored in a second channel. Sweeping the voltage range in steps of 0.1 V permits us to distinguish between X-rays of various energies. If the X-ray photons are counted by energy, we can obtain I, the X-ray intensity at given energy. This permits us to plot I vs. wavelength (energy), which gives us an energy spectrum of the XRF from the sample. An EDXRF spectrum is in the form of a histogram, usually plotted as "counts" on the y-axis, where counts means the number of photons counted in a given channel, vs. energy on the x-axis. In practice, an EDXRF is equipped with a pulse height analyzer with many channels and complicated signal processing circuitry. A typical multichannel pulse height analyzer may have 1024 channels, each corresponding to a different energy interval.

Resolution in a semiconductor detector EDXRF system is a function of both the detector characteristics and the electronic pulse processing. The energy resolution of semiconductor detectors is much better than either proportional counters or scintillation counters. Their excellent resolution is what makes it possible to eliminate the physical dispersion of the X-ray beam; without the energy resolution of semiconductor detectors, EDXRF would not be possible.

While Si(Li) is still the most common semiconductor detector material for laboratory-based EDXRF systems, Ge(Li), high-purity Ge, mercuric iodide (HgI_2), and compound materials such as GaAs and CdTe have been used. The lithium-drifted detectors must be maintained at liquid nitrogen temperatures at all times, to minimize noise and to prevent Li migration in the crystal. High-purity Ge and the other compound materials do not required constant cooling. Signal-to-noise is often improved by operating these detectors at subambient temperatures, but mercuric iodide detectors work well at ambient temperatures. This makes mercuric iodide an excellent detector for portable, handheld EDXRF
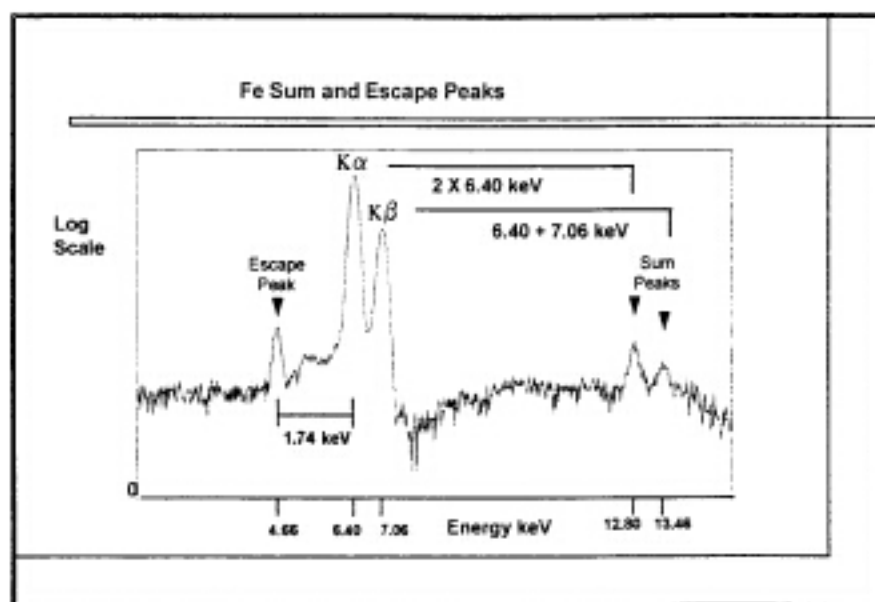
Figure 8.31 Artifacts in an EDXRF spectrum. The spectrum of pure iron, measured with a Si(Li) detector, shows a peak lower in energy than the Fe K_α peak by an amount exactly equal to the energy of the Si K_α line. Some of the Fe photon energy is transferred to the Si detector atoms; the amount of energy absorbed by an Si atom has *escaped* from the Fe photon. This type of peak is called an escape peak. Sum peaks also appear in EDXRF spectra when two intense photons arrive at the detector simultaneously. A sum peak from two K_α photons is shown along with a sum peak from one K_α and one K_β photon. [Courtesy of Thermo ARL (www.thermoARL.com).]

analyzers where carrying around a large dewar (a fancy thermos bottle) of liquid nitrogen is not practical and for the X-ray spectrometers sent on space missions, where refilling the liquid nitrogen dewar every week is not possible.

8.2.7.2. Escape Peaks and Sum Peaks

Spectrum artifacts may appear in the energy dispersive spectrum. These are peaks that are not from elements in the sample. The Si escape peak, from the Si K_α line, results in an artifact peak 1.74 eV lower than the parent peak when a Si(Li) detector is used. Such an escape peak is shown in the EDXRF spectrum of an iron sample in Fig. 8.31. Similar escape peaks at different energies appear for Ge if a Ge detector is used.

Sum peaks in the EDXRF spectrum occur when two high-intensity peaks arrive so close in time that the signal processing electronics cannot separate them. A single peak is registered at an energy that is the sum of the two peaks. Figure 8.31 displays this type of artifact. The major elements in the sample (e.g., iron in steel) are usually the source of the sum peaks.

Most EDXRF systems come with software that automatically corrects for escape and sum peaks.

8.3. ANALYTICAL APPLICATIONS OF X-RAYS

There are three distinct fields of X-ray analysis: X-ray absorption, which varies with atomic weight; XRD, which depends on the crystal properties of solids; and XRF,