NEW INSTRUMENTS AND MEASUREMENT METHODS

Color contrast in scanning electron microscopy

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A new procedure is developed for the investigation of luminescent solids in a scanning electron microscope operating in the cathode luminescence regime. The optical radiation produced when the electron beam interacts with the surface of the investigated substance is registered and used as a video signal to produce a color image corresponding to the emitted spectrum in the visible region. The use of color contrast greatly increases the information content over the hitherto used amplitude contrast in black and white. This process is effected in two ways. In the first, sequential photography is used with a single receiver with interchangeable light filters (blue, red, green), so that black and white color-separation photographs are produced. The color photograph of the investigated surface is then obtained by additive synthesis. In the second method, three receivers with filters are used, and the color image is produced by a three-channel amplification system directly on the screen of a color monitor. The second method offers considerable advantages over the first, permits observation of both static and dynamic processes, yields immediate information on the chemical and structural state of the surface, and permits direct photography on color film. With minerals as examples, it is shown that color cathode luminescence (CCL) permits observation of the zone character of the structure, grain boundaries, regions where certain elements are substituted for others, growth zones, etc. CCL makes it possible to analyze manufacturing-technology defects in color TV tubes and to reveal imperfections in heterojunctions and diode structures. When used in the analysis of soil objects, it is possible to obtain a qualitative picture of the distribution of microinclusion, as well as their partial identification.

Electron bombardment of a solid placed in a scanning electron microscope (SEM) may produce images of the object as a result of a large number of physical phenomena. Secondary electron emission (SEE), optical cathode luminescence, and x rays are used to obtain images in a scanning electron microscope.

Secondary electron emission yields mainly information on the microgeometry and cathode luminescence (CL), owing to the excitation of an optical spectrum determined by the band structure of semiconductors and dielectrics, a structure sensitive to the chemical composition of the substance. X rays containing a characteristic component yield information on the presence of individual elements in the sample[1-4].

CL and x rays[5] are not alternatives, but complement each other. It is important to know not only that certain elements are present, but also the chemical compounds contained in the sample. These local data are required in particular, for biology, mineralogy, and the physics of dielectrics and semiconductors. This information can be extracted from CL in the visible and in the adjacent ultraviolet and infrared regions of the spectrum. The diagnostic capabilities of CL are realized in two ways:

1) By producing an image (a) in black and white (b/w), (b) in color, and (c) in "quasicolor."

2) By extracting the optical signal from the x-ray microanalyzer or the SEM to a spectral instrument.

Both methods can be reduced to a single system that permits a survey of the entire image and local observation of the spectrum. An x-ray microanalyzer provided with an optical microscope with which to view the object bombarded by an electron beam has made it possible to observe color CL directly[6, 7]. Owing to the use of microanalyzer rather than an SEM, the resolution was of the same order[1]. Extraction of the CL signal was used in a number of studies[9-11]. The use of quasicolor, i.e., of an artificially colored image (using a color filter) to obtain a three-dimensional image is described in[12], where other interesting applications are also proposed.

We have developed two systems[14] for obtaining colored cathode luminescence (CCL) images, a single-channel system containing in part the elements of the devices of[12, 13], and a new multichannel system, offering many advantages over the single-channel systems and over the methods described in[12, 13]. In the single-channel system "a" (Fig. 1), the following aggregate of operations is performed: 1) three "filtered b/w images are obtained by using three color filters; 2) these three b/w images are photographed in sequence from the screen of the TV tube; 3) three optical projectors, through appropriate color filters, "color" simultaneously the previously obtained b/w negatives. The obtained (synthesized) image is finally photographed on color film.

In the multichannel system "b" (Fig. 2) there are no less than three channels for the CCL, with direct extraction of the optical signal to the screen of a color TV tube. Although each photomultiplier is adjusted to cover a definite section of the spectrum, a system for double color correction is nevertheless required, 1) by color temperature (by acting on the electron guns of the TV tube) and 2) by means of the dynamic amplification system (left-hand side of Fig. 2). The complicated color-correction system is necessary because CCL calls for stringent requirements on the intensity and

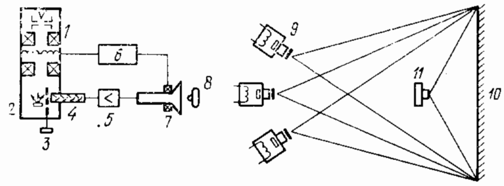

FIG. 1. Single-channel system for obtaining color images in an SEM by additive synthesis of color-separated images. 1—SEM column, 2—object, 3—interchangeable filters, 4—photomultiplier, 5—amplifier, 6—sweep generator, 7—TV tube, 8—photographic camera, 9—diapositive projectors with filters, 10—screen, 11—color-film camera.

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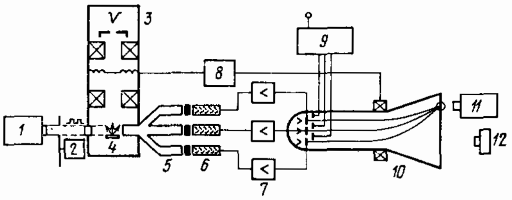

FIG. 2. Functional system for obtaining color images in an SEM using a color video-control system. 1—Light source, 2—light-beam chopper, 3—electron-optical section of SEM, 4—object, 5—light pipes, 6—photomultipliers with filters, 7—amplifiers, 8—sweep generator, 9—color-correction block, 10—color TV tube, 11—pyrometer, 12—color-film camera.

the hues of the color (owing to noise due to the filter and to the matching of the color sensitivity of the photomultipliers to other elements of the SEM).

The main advantage of system "b" is that the image is produced simultaneously in all the colors. This permits observation of both static and dynamic phenomena. There is no need for changing filters and taking intermediate photographs as in case "a." Direct observation on the screen is possible, and if desired color photographs of the screen can be taken. To ensure reception of weak and undistorted signals, the system "b" contains also other devices to set the sample at any desired temperature, to shield the object against polymer films, to remove the charge, for electron stroboscopy, and to separate the signals from the noise. The system was used to test the interesting properties of gallium phosphide. A CCL picture of a GaP diode at room temperature reveals a green band identifying the p-region, shows a dark p-n junction, a bright n_+ section, and again a dark p-n junction over the n region. When the temperature is lowered to that of liquid nitrogen, a new red band appears near the p-n junction, as well as orange and green bands that are located in accordance with the optimum of the doping impurity. This type of a dynamic picture can be observed by using the system "b."

Interesting SEM studies were made of TV screens consisting of color triads. A synthesized image obtained by us has revealed individual circles whose colors were not spectrally pure, so that they could affect adversely the image quality. Examination of rock specimens containing scheelite (blue) and molybdos scheelite (yellow) crystals were observed with adjacent sections (dark) of molybdenite. Distinct color differentiation was clearly observed at 1000x magnification e.g., a blue edge of pure scheelite surrounding a dark molybdenite scale, and both surrounded by a light-yellow depleted region of molybdoscheelite. So distinct a picture of the zone character of substitution has never been observed before with a polarization microscope., owing to the close values of the refractive indices of the scheelite and the molybdoscheelite. Secondary electron emission, while well suited for microgeometry, is relatively insensitive to chemical composition. CL in the b/w variant can reveal certain structural features of a sample[17]. CCL, as can be demonstrated[18] with polished unetched rock minerals, display clearly the contacting quartz and felspar (blue) crystals, which contain inclusions of late-magmatic albite (yellow).

As stated above, CCL and micro-x-ray analysis determine different components of the sample. The correlation between the two methods was examined[16] with impurity-containing sphalerite ZnS as an example. The table shows the data obtained with a micro-x-ray analyzer for two groups of sphalerite, one containing manganese and cadmium impurities, but no iron, while the other has cadmium and iron, but no manganese. CCL images of a sample of the second group has revealed green regions corresponding to ZnS and bright yellow regions of Cd. Iron, which quenches the CL, produce a unique green region alternating with dark sections. The cadmium is quite pronounced, since it is known that it enhances the CL. The image shows clearly both the regions where the ZnS has impurities, and the impurity boundaries.

Results of x-ray microanalysis of sphalerite samples (wt. %)

Elements	First group of samples		Second group of samples		
	№ 8040	№ 8066	№ 9043	№ 9056	№ 8467
	Average of four analyses			Average of two analyses	
Zn	62,5	61.4	65.9	66.2	66.9
Fe	—	—	0.5	0.3	0,1
Mn	1.5	2.7	—	—	—
Cd	3.0	3.2	0.5	0,5	0,1
S	33.0	32.7	33,1	33.0	32,9

A cycle of CCL investigations of soil which is a heterogeneous system of different chemical and mineralogical substances, was carried out under natural conditions to establish its local properties and composition. Images obtained by us have shown, for example, the manner in which a felspar grain (blue-white) is acted upon by the surrounding mass of calcite ($CaCO_3$) (green). The boundary between them is diffuse, the CL of the felspar is uneven, thus indicating the presence of a region of varying chemical composition. We thus observe the process of isomorphic substitution, which cannot be observed by optical means. The CCL picture of a ZnS crystal reveals at liquid-nitrogen temperature a variety of colors. We note that diffuseness in the picture may depend on the periods of the CL quenching and of the sweep over the SEM screen.

By examining a GaP crystal with carefully measured impurities, we have established that the sensitivity of CCL is higher by at least two orders than that of x-ray microanalysis.

Thus, the information capacity of CL observed on the TV tube screen is greatly increased by replacing b/w by color contrast. This is due to the high sensitivity of the eye, which can distinguish between 1000 hues. The spatial resolution of the CL, according to[4], can be of the order of 0.1 μ. The chemical-composition data obtained with CCL were monitored not only with luminescence and polarization microscopes, but also by a separate chemical analysis. The luminescence method[20] is well known in ordinary optics. In the CCL regime this method, in conjunction with various SEM procedures, offers, as shown here, many new possibilities that will be diligently developed.

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