The application of high-resolution scanning electron microscopy to inorganic materials

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This paper is an overview of the effect of scanning electron microscope (SEM) operational parameters on the microstructure of inorganic materials. Examples are shown by selecting different parameters of voltage, detector and working distance that are common but hard to be optimized for daily operations. These will help to get the ideal as well as real morphology of non-conductive inorganic materials using SEM.

Keywords SEM; Operational parameters; Microstructure; Inorganic materials

1. Introduction

Scanning electron microscope (SEM) is an important tool for materials science research due to its simple operation and data interpretation as well as the strong ability to resolve surface details at micro- and nano-meter levels. One of the development trends in SEM techniques is to get high-resolution images regardless of the voltage. The ultrahigh-resolution at low-voltage SEM has been available with the development of new emitter and minimising chromatic aberration. The major attraction of high-resolution SEM resides in its high surface sensitivity as the size and range of interaction volume of electrons in the sample dramatically shrink when the primary electron beam voltage decreases [1-3]. Therefore, it is critical to select optimal SEM operation conditions to get the real surface details of materials. In this paper, the effects of major SEM operational parameters on the microstructure of several inorganic materials are discussed.

2. Effect of accelerating voltage

2.1 Nano particles

Fig. 1 shows the surface morphology of nano Y2O3 particles at different accelerating voltages. The charging is observed on particle surfaces at 5 kV, showing smooth surface of the Y2O3 particles 200 - 300 nm in size (Fig. 1a). Interestingly, some nanosize pores occur on the particle surfaces when the voltage drops to 3 kV as depicted in Fig. 1b. More details of the pore size and distribution of Y2O3 particles are obtained at 2 kV whose SEM image is shown in Fig. 1c and its real surface morphology is obtained at 1 kV with more than 90 % surface area occupied by mesopores approximately 10 nm in size, as shown in Fig. 1d.
Fig. 1  SEM images showing the surface morphologies of nano Y₂O₃ particles at different accelerating voltages: a) 5 kV; b) 3 kV; c) 2 kV; and d) 1 kV.

2.2 Graphene

Graphene is a monolayer material composed of carbon atoms in a honeycomb lattice. Due to sp² hybridized bonding, graphene has a high degree of chemical and mechanical stability. Together with the peculiar electronic properties from its two-dimensionality (2D), graphene has attracted significant attention from materials scientists. The successful fabrication of graphene in 2004 has demonstrated many fascinating physical properties of this monolayered 2-dimensional (2D) material [4,5].

Fig. 2 shows the surface morphology of copper (Cu) fully covered by graphene. The contrast between different parts of the surface area is not prominent at 5 kV (Fig. 2a), resulting in difficulties in understanding the contribution of monolayer graphene to contrast. With the decrease in voltage, the contrast between graphene with different thickness gradually turns prominent (Figs. 2b, 2c) and the best contrast is observed at 0.5 kV whose SEM image is shown in Fig. 2d. In the three kinds of contrast, the brightest one corresponds to the monolayer graphene and the darkest one corresponds to the graphene consisting of five layers (Fig. 2d), as confirmed by Raman scattering spectroscopy. The gray area indicates the graphene with 2 - 4 layers. Detailed information of thickness can be obtained from BSI images using an appropriate voltage.

Fig. 2  SEM images showing the surface morphology of Cu substrate covered by multi-layered graphene at different voltages: a) 5 kV; b) 2 kV; c) 1 kV; and d) 0.5 kV.

Scientific community shows increasing attention towards composite ceramic materials by combining the advantages of ceramics and graphene such as Al₂O₃/graphene composites. The key problem encountered when preparing such composite is related to the good attachment of Al₂O₃ particles to graphene sheet. Fig. 3 shows the morphologies of Al₂O₃/graphene composite at different voltages. Few Al₂O₃ particles are observed at the outside of graphene and barely
surrounded at 1 kV, as shown in Fig. 3a. However, the graphene is translucent at 5 kV and a large number of Al₂O₃ particles are internally surrounded (Fig. 3b), suggesting the good combination of graphene and Al₂O₃ particles. Therefore, a high voltage may not be good for SEM observation of graphene and an optimal voltage is needed for different observation purposes.

![SEM images showing the morphology of Al₂O₃/graphene composite at different voltages: a) 1 kV and b) 5 kV.](image)

**Fig. 3** SEM images showing the morphology of Al₂O₃/graphene composite at different voltages: a) 1 kV and b) 5 kV.

2.3 Mesoporous materials

Recently mesoporous materials with a pore size range of 2-50 nm have attracted substantial interest due to their potential applications as catalyst, adsorbent and electrode for super capacitor [6-8]. The method most commonly used for pore characterization of mesoporous materials is transmission electron microscope (TEM). However, TEM images often provide projected and sometimes confusing microstructure information because its accelerating voltage is usually more than 100 kV at which the temperature increases with incident electron, resulting in the damage to the pore structure. In contrast, SEM, particularly the high-resolution low-voltage SEM, is advantageous in terms of easy sample preparation and observation of the top surfaces at low voltage. It allows characterization of the orderly structure with relatively simple preparation. SEM characterization of mesoporous materials is mainly confronted with charging problems of insulating frameworks and structural collapse due to electron beam irradiation, which are also encountered in TEM applications. SBA-15 powders are common mesoporous materials with ordered single-dimensional hexagonal pores.

Fig. 4 shows the typical two-dimensional hexagonal pore shape of SBA-15. The structure should be shown as hexagonal pores when the incident electron beam is nearly perpendicular to the mesoporous channels and as a linear structure when the electron beam is nearly parallel to the mesoporous channels. Both structures should be shown on the surface of SBA-15 samples by SEM. Fig. 5 shows the surface morphology of SBA-15 at different accelerating voltages. It is found that, only the hexagonal pores emerge when the linear structure is shown as a smooth area at 10 kV, as depicted in Fig. 5a. Both hexagonal pores and linear structure are shown at 1 kV when the electron beam is incompletely perpendicular to the mesoporous channels (Fig. 5b). When the electron beam is approximately parallel to the channels, the linear structure is clearly shown at 1 kV (Fig. 5c).

![Schematic diagram of the typical mesoporous structure of SBA-15.](image)

**Fig. 4** Schematic diagram of the typical mesoporous structure of SBA-15.
As electron-sample interactions are restricted to the near-surface regions of the sample at low voltage, SEM images used for revealing fine structures can easily be affected by surface features. In contrast, the interaction volume enlarges with the increase in accelerating voltage. Consequently, SEM signals from different depths of interaction volume will overlap, resulting in the absence of detailed structure on the surface such as the linear structure.

3. Effect of detectors

Currently the mainstream field emission SEM (FESEM) is generally provided with two secondary electron detectors i.e., upper detector and lower detector, as shown in Fig. 6. The upper secondary electron detector is mounted over the objective lens and the secondary electrons pass through a magnetic field in the centre of the objective lens. According to the Fleming's left-hand rule, the secondary electrons can only be caught finally by the upper detector under a magnetic field force. The low secondary electron detector with a small secondary electron capture angle is directly mounted under the objective lens. In this study, we observe different samples using the upper and low secondary electron detectors to explore the detector effect on FESEM image.

Being mounted under the objective lens, the lower detector has a small secondary electron capture angle. Various semaphores are received from different directions at different heights with different contrast. Therefore, images taken...
by the lower detector have a stronger tri-dimensional effect than that of taken by the upper detector. Fig. 7 shows the morphology of a ZnO thin film observed using the upper detector (Fig. 7a) and the lower detector (Fig. 7b). The images were taken from the same area of identical samples using the same accelerating voltage and electron beam current conditions. It is clear that as mounted at a low angle, the lower detector has a small secondary electron capture angle. Consequently, the crystal plane receives various SEM semaphores from different directions with a large-contrast high tri-dimensional effect and obvious crystal edges.

Fig. 7  SEM images obtained with different secondary electron detectors showing the morphology of ZnO thin film: (a) the upper detector and (b) the lower detector.

Fig. 8 shows morphology of bovine enamel immersed in citric acid solution (pH 1) for 5 min. When the lower detector is mounted at a small angle, it shows more evident height fluctuation of enamel columns. The image pairs Figs. 8a, 8c and 8e are taken by the upper detector and Figs. 8b, 8d and 8f by the lower detector. The image pairs of Figs. 8a & 8b, Figs. 8c & 8d and Figs. 8e & 8f are taken from the same area of identical samples using the same accelerating voltage and electron beam current conditions. Apparently, the tri-dimensional effect of images taken by the lower detector is stronger than that of the upper detector during morphological characterization of the same sample under the similar testing conditions.
Fig. 8  SEM morphological images of bovine enamel using different secondary electron detectors: (a) the upper detector, x 1000; (b) the lower detector, x 1000; (c) the upper detector, x 5000; (d) the lower detector, x 5000; (e) the upper detector, x 50000; and (f) the lower detector, x 50000.

The signals captured by the secondary electron detectors are mainly secondary electron signals, which involve certain backscattered signals. However, as mounted at different heights, the upper detector receives high-angle backscattered signals and a few low-angle backscattered signals, whereas the lower detector only receives a few low-angle backscattered signals. Therefore, the images captured by the upper detector have more composition information. The schematic diagram of backscattering signals collected from different angles by upper and low secondary electron detectors is shown in Fig. 6. Secondary electron signals are mainly surface morphological signals with a strong edge effect and high-angle backscattering signals mainly show composition contrast. Despite of the weak composition contrast, low-angle backscattering signals can reduce the edge effect.

The lower detector mounted at a low position is insensitive to charge signals. Thus, images can generally be taken when the sample discharges slightly. Fig. 9 shows SEM morphological images of spray graduated SiC balls respectively taken by the upper and lower detectors. The sample neither conducts electricity nor sprays. The same area of identical samples is selected for taking images under the same accelerating voltage and electron beam current conditions. As shown in Fig. 9a, the sample discharges and seriously affects surface morphological characterization of SiC balls when the upper detector is used for signal capture. However, as the lower detector is less sensitive to charge signals than the upper detector, the charging is evidently weakened and the surface morphology of SiC balls is clearly represented when the lower detector is used to capture signals (Fig. 9b).

Fig. 9  SEM images obtained by different detectors showing the spray-graduated SiC balls (non-conductive and not-sprayed): a) the upper detector; and b) the lower detector.

4. Effect of working distance

It is well known that the working distance can substantially affect the quality of SEM images. In general, a short working distance results in a high-resolution image, whereas a long working distance causes a large depth of field. Fig. 10 shows the relationship between the working distance and depth of field. With the same sample of the same magnification, a 1.5-times increase in the working distance results in an approximately double increase in depth of the field.
Fig. 10  Relationship between working distance and depth of field.

Fig. 11 shows the fracture morphology of identical Cu/Se alloy observed at different working distances. With a working distance of 2 mm, the focus area is clear with obvious defocus observed on the top left of the image (Fig. 11a). This indicates the significant height difference between the focus and defocus areas. The partial defocus issue is fixed when the working distance increases to 5.6 mm (Fig. 11b) and completely disappears at a working distance of 10 nm (Fig. 11c). These indicate that the increase in working distance can substantially improve the depth of field to produce high-resolution image at a relatively low magnification.

The use of long working distance and large depth of the field also yield other useful information. A long working distance corresponds to a large rotation angle, thus allowing the collection of more 3D information. Fig. 12 shows the surface morphology of a semi-conduct device (×200). With an aperture angle of zero, this semi-conduct device appears to be normal with no deformation (Fig. 12a). When the working distance exceeds 25 mm, the device is tilted at 45° and shows substantial deformation at edge of the image (Fig. 12b). This demonstrates that the semi-conduct device has certain security risks.
Fig. 12 SEM images showing the surface morphology of a semi-conduct device pattern at different aperture angles: a) 0°; and b) 45°.

5. Summary

SEM plays an indispensable role in materials sciences research. Along with the development of SEM techniques, the resolution of SEM images and the amount of microstructure information have been substantially improved. However, the selection of operational conditions, particularly the accelerating voltage, is of significance to the collection of accurate information of the microstructure. At a low accelerating voltage, the surface morphology of materials can easily be observed with relatively low resolution, whereas at a high accelerating voltage the electrons have a deeper penetration depth, yielding more information of surface morphology with relatively high resolution.

The upper and low secondary electron detectors of FESEM have different functions. The former can be used to take highly-magnified images that are potentially required to show the composition difference, whereas the later can be used to enhance the 3D effect of SEM images and reduces the charging. Ideal SEM images can be obtained only when the detectors are selected according to the specific test requirements.

The increase in working distance can improve depth of the field while elevating the rotation angle, further yielding more 3D information. However a long working distance also reduces the resolution of SEM images, this is suitable for use of low magnifications. In summary, ideal SEM microstructure of inorganic materials can only be obtained when optimal operational parameters are selected according to multiple factors such as the sample type and test requirements.

References