HITACHI SCIENTIFIC INSTRUMENT
TECHNICAL DATA
SEM

SHEET NO. 103

SUBJECT: ELECTRON MICROSCOPY OF COMPOUND MATERIALS USING LOW VOLTAGE STEM MODE OF THE S-5200 ULTRA-HIGH RESOLUTION SEM

CONTENTS

1. INTRODUCTION

Various combinations of materials which have different compositions or hardness have been studied for development of advanced (functional) new materials. For microscopy of these materials, specimen preparation is a mandatory requirement. In addition to conventional ultra-microtomes, focused ion beam (FIB) systems have been extensively used. The FIB systems are advantageous in that they allow specimen preparation without giving mechanical forces to the specimen. A low voltage scanning transmission electron microscopy technique has been applied for observation of high polymer materials[1] and it has been proved to be useful due to high angle scattering of electrons which allow good imaging contrast. This technique has also been used for microscopy of semiconductor devices[2] in combination with FIB systems and microscopy of biological sections[3]. We have studied some functional compound materials including high polymer or organic materials using the S-5200 ultra-high resolution SEM. We report here on some microscopy results of inner structures made visible with the low voltage STEM technique.

Fig. 1 A general view of the S-5200 ultra-high resolution SEM

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2. FEATURES OF STEM MODE OF THE S-5200

In the STEM mode of operation, electron beam scattering in the specimen is the primary cause of scattering contrast available for the image. When a beam of electrons strikes a specimen, beam broadening takes place which is expressed in the following equation[4]:

$$b = b_0 + 625 \times 107 \cdot Z/E_0 \cdot (\rho/A)^{1/2} \cdot t^{3/2}$$

where b: electron beam broadening (nm)
A: atomic weight
b_0: probe diameter of incident electron beam (nm)
E_0: accelerating voltage (kV)
Z: atomic number
ρ: specimen density (g/cm^3)
t: specimen thickness (×10 nm)

From this equation, the scattering contrast is proportionate to specimen density and atomic number and inversely proportionate to accelerating voltage. The low voltage STEM imaging at accelerating voltages of 10 - 30 kV) is useful for specimens composed of low atomic number elements and low density specimens. Fig. 2 shows an example of STEM image of a high polymer material recorded at an accelerating voltage of 10 kV. White polymethylmethacrylate (PMMA) particles in black polystyrene (PS) are clearly observed with good imaging contrast. The low voltage STEM mode of the S-5200 makes small differences in specimen density and compositions clearly visible in bright and dark contrast. It achieves a high resolution of 0.6 nm at 30 kV.

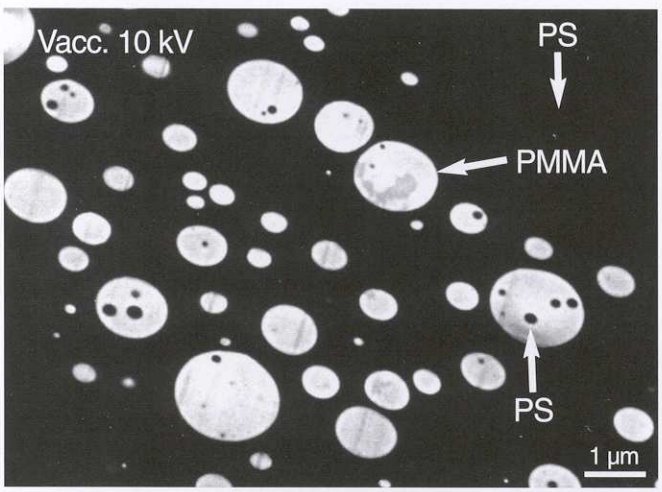


Fig. 2 A low voltage STEM image of a high polymer (PMMA/PS) specimen

3. APPLICATIONS

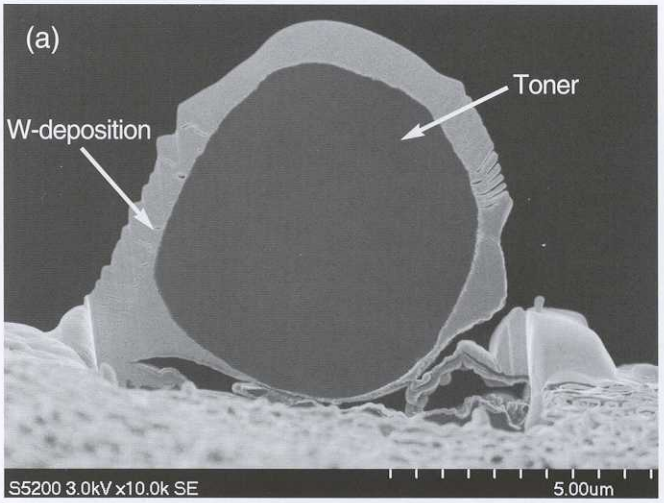
Table 1 shows specimens, preparations, and operating conditions of the FIB system (when applied).

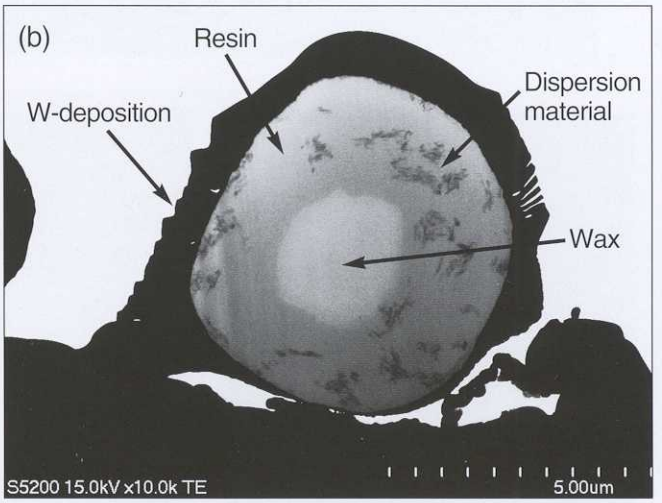
Table 1

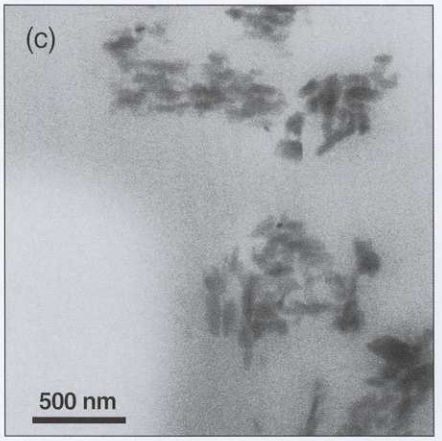
Specimens	Preparations	Operating conditions of the FIB system
1. Toner	Pt-coating at about 20 nm for electron conductivity	After tungsten deposition at about 1 µm, the specimen was thinned at about 0.1µm.
2. Polymer	Dispersed on carbon/grid	
3. DVD-RAM	Carbon and Pt-coating at a thickness of 10 nm and 20 nm respectively for electron conductivity	A piece of specimen of about 15 × 15 × 5 µm was cut out using a micro-sampling technique. After carbon deposition at about 1µm, the specimen was thinned at about 0.1 µm.
4. Coat/print/high polymer layer on aluminum substrate		

3.1 Microscopy of toner particles

Fig. 3 shows microscopy results of polymerized toner(cyan-color) used on laser color printers. The specimen was thinned at about 1 μm using the FIB system. The toner particle is designed about 6.5 μm in diameter and contains wax inside. Fig. 3(a) is an SEM image which shows the toner particle has been thinned without deformation. Fig. 3(b) is a STEM image recorded at 15 kV and it shows resin, wax and dispersion materials clearly separated. Inner structures are clearly visible. The low voltage STEM images are useful for observation of organic materials such as resin and wax which have only a slight difference in specimen density. Fig. 3 (c) is an enlargement of a portion of Fig. 3(b) showing the dispersion material. Magnification is ×50,000. It shows the dispersion material very closely. Fig. 3(d) is an X-ray mapping image showing that the toner contains copper.







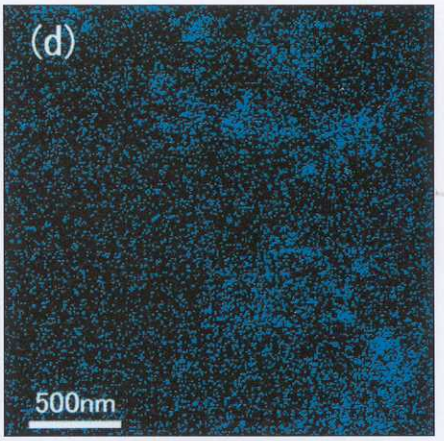
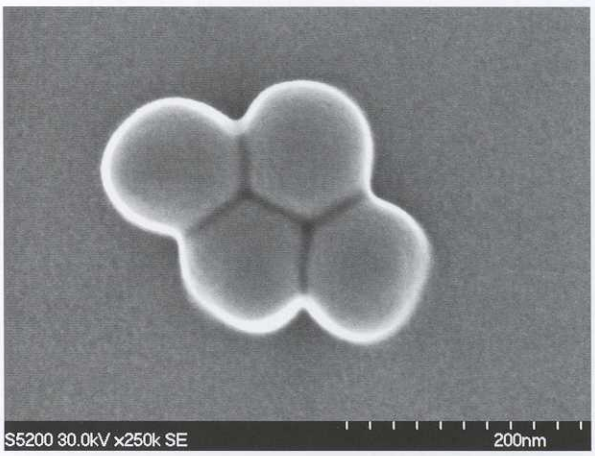


Fig. 3 Observation of toner
(a) Low magnification SEM image
(b) Low magnification STEM image
(c) High magnification STEM image
(d) X-ray mapping image

3.2 Microscopy of polymers

Fig. 4 shows SEM/STEM observation and X-ray analysis results of acrylic/Si-polymer dispersed on specimen grid. This polymer is used as an additive for paint. Fig. 4(a) is an SEM image recorded at ×250,000 and shows the particle at about 80 nm. Fig. 4(b) is a STEM image recorded at 30 kV and it shows the inner specimen or core-shell structures. Fig. 4(c) are X-ray mapping images showing silicon and oxygen presence in the core-structures and the organic material just outside the polymer.

(a)



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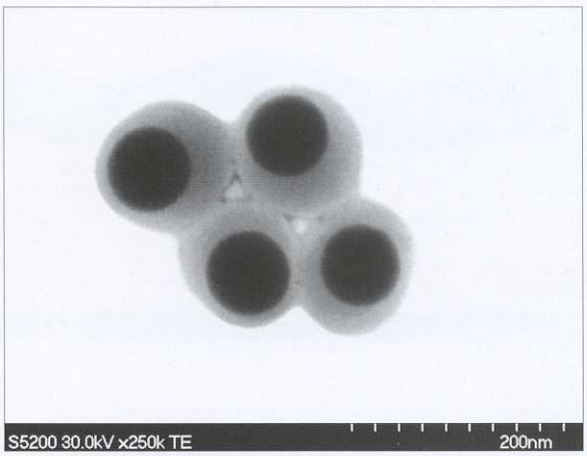

(c)

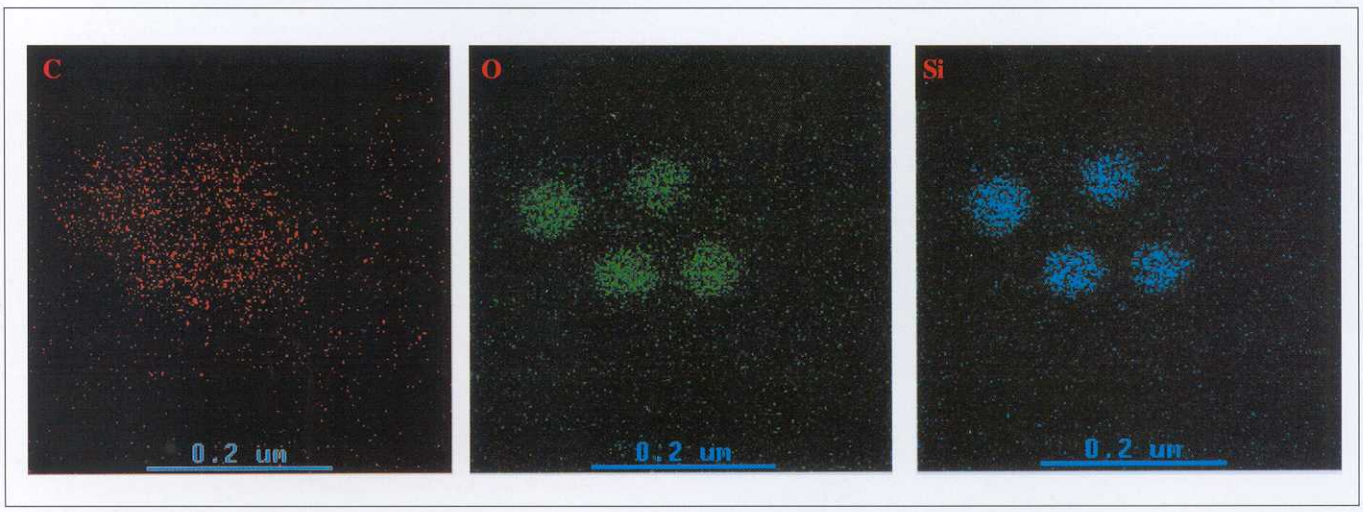

Fig. 4 Microscopy of polymers
(a) SEM image
(b) STEM image
(c) X-ray mapping image

3.3 Microscopy of DVD-RAM

Fig. 5 shows a commercial 9.4Gb DVD-RAM, FIB thinned to about 0.1 μm thick. Fig. 5(a) is a STEM image recorded at ×50,000 and at an accelerating voltage of 30 kV. It shows 7-layer structures thinned without damage. The masked area was magnified at about 400,000 times which is shown in Fig. 5(b). It shows a layer structure of about 5 ~ 6 nm which is in the recording layer. Fig. 5(c) is an X-ray mapping image. It shows a structure of a few nm recognized by X-ray analysis even with a low voltage STEM technique.

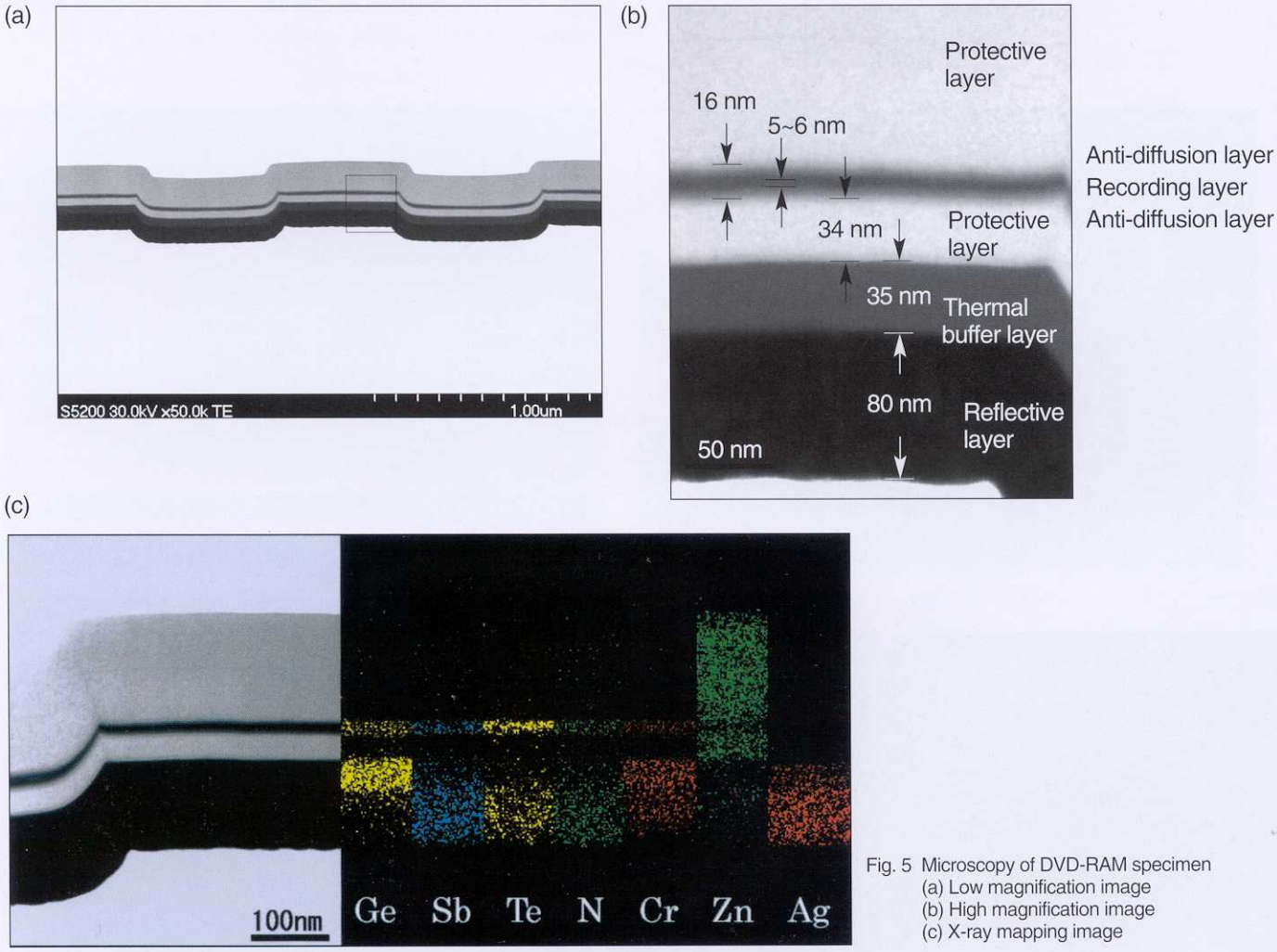

Fig. 5 Microscopy of DVD-RAM specimen
(a) Low magnification image
(b) High magnification image
(c) X-ray mapping image

3.4 Microscopy of a print layer on aluminum substrate

Aluminum cans have been widely used for drinking water and other beverages. These cans are composed with aluminum layer, white coat layer, printing layer (green color area was examined) and polymer layer. Ultramicrotomes have been used for specimen preparation up to this time. It has been a time-consuming work. We have used here a new micro-sampling technique with the FIB. A small piece of specimen of about 15 μm× 15 μm×5 μm was cut out first. It was then thinned to a thickness of about 0.1 μm. This technique allows specimen preparation quickly. Figs. 6 (a) and (b) show STEM images recorded at 30 kV. Fig. 6 (a) is a low magnification image showing 4-layer structures. Fig. 6 (b) is a high magnification image of the print area. It shows 3 kinds of particles; fine particles of about 10 nm, medium 50 nm particles, and large 200 nm particles. Fig. 6(c) show X-ray mapping images of these particles. Major elements composing these particles have been detected. They are silicon, copper, and chlorine.

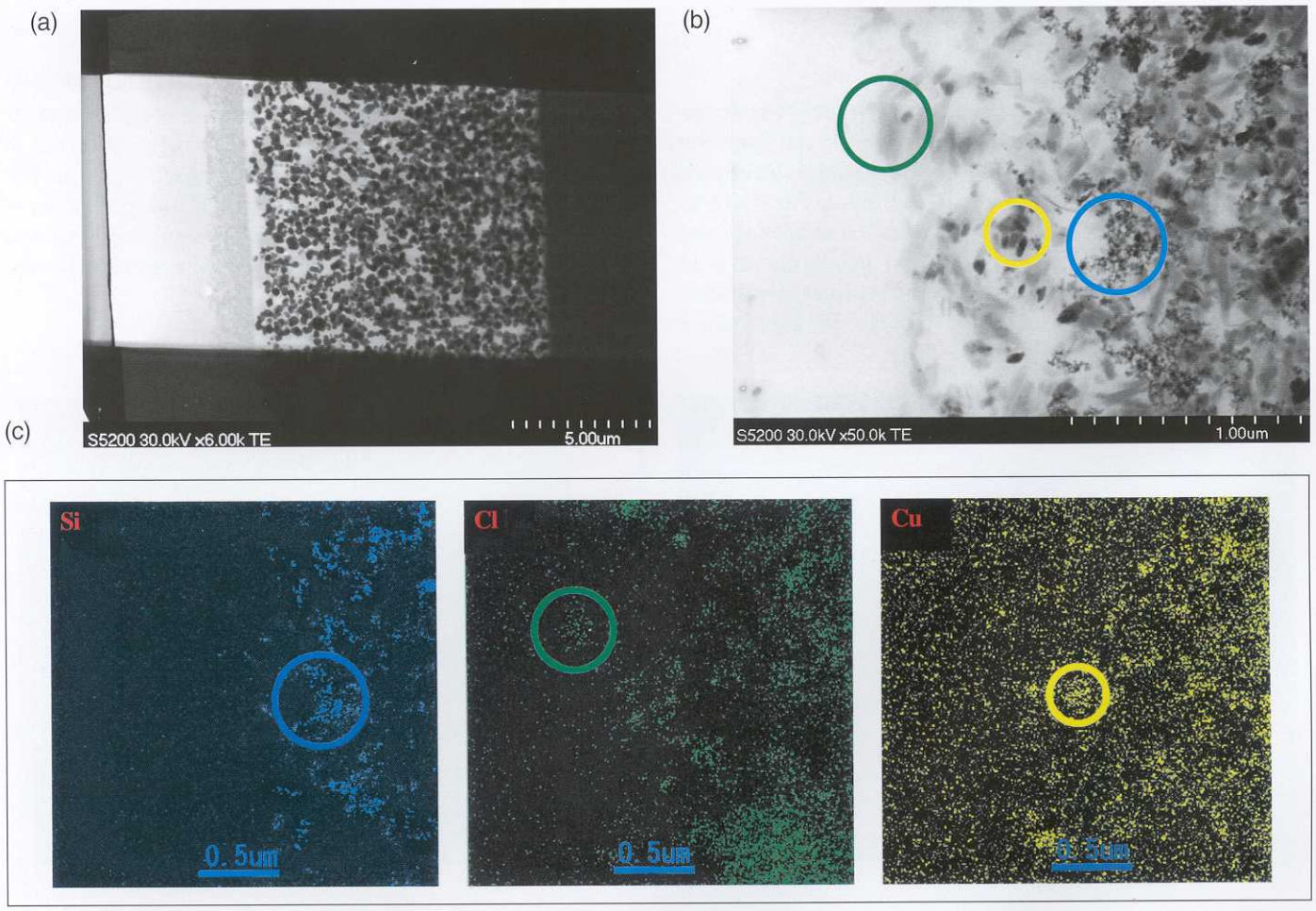

Fig. 6 Microscopy of a print layer on aluminum substrate
(a) Low magnification image, (b) High magnification image, (c) X-ray mapping image

4. CLOSING REMARKS

Low voltage (15 ~ 30 kV) STEM mode of the S-5200 ultra-high resolution SEM allows imaging of organic materials and compound materials which include polymers. It makes inner structures clearly visible with good contrast and a good S/N ratio. The linkage function[2] with the FIB system and the micro-sampling attachment allow quick specimen preparation for those specimens which have been difficult and time-consuming with conventional techniques. A high angle X-ray take-off geometry available with the S-5200 allows X-ray microanalysis of light elements using compound materials as demonstrated here. We trust that the S-5200 will be found useful for microscopy of surface and inner structures of various materials in the future.

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