My Research along with High-Resolution, High-Voltage Electron Microscopy

Shigeo HORIUCHI

(1969-1999) National Institute for Research in Inorganic Materials (NIRIM), Japan

(1999-2003) Cooperate Research Laboratory, Mitsubishi Gas Chemicals, Japan

(2003-at present) Korea Electrotechnology Research Institute (KERI), Korea Correspondence:

s.horiuchi@ibaraki.email.ne.jp

I have engaged in the research on the development of high-resolution, high-voltage electron microscope (HR-HVEM) and its application to materials science for 35 years. In this lecture I would like to introduce it.

A. Construction of HR-HVEM

1. 1st HR-HVEM

In 1976 a new HR-HVEM was constructed at NIRIM [1]. The HVEM had the point-to-point resolving power of 2.0Å at the accelerating voltage of 1000kV under the equipment of the specimen tilting stage of 45°. This was the first achievement of high-resolution type of HVEM in the world. For comparison, the accelerating voltage of a conventional transmission EM at that time was 100kV with the resolving power of about 4Å. The HR-HVEM enabled us to visualize individual metal atoms in ceramic materials for the first time.

Besides, we have contributed to the development of the optical-imaging theory, e.g. the effect of the specimen thickness on the so-called Scherzer's resolution limit has been clarified, with aid of computer calculation on the quantitative analysis of the diffraction intensity [2].

2. 2nd HR-HVEM

In 1987 high-Tc superconductors were discovered. We considered it important to analyze the arrangement of oxygens in supuerconducting oxides by means of HR-HVEM. According to the computer simulation it was clear that the point-to-point resolving power of 1.0Å is necessary to visualyze oxygens in HR-HVEM images. We have then tried to increase the resolving power by

further improving the electron lens system at the accelerating voltage of 1300kV. We have finally succeeded in constructing the aimed HR-HVEM in 1990 [3,4].

B. Application of HR-HVEM to materials science

1. Structure analysis

Crystal structure analysis is what should be done first in materials science. Our HR-HVEM has been utilized very usefully in the structure analysis of ceramic crystals. We have developed a new method of structure analysis by means of HR-HVEM, i.e. the three-dimensional structure analysis based on the combination of high-resolution structure images taken from two directions [5]. This method has been successfully applied especially to the so-called layer structure, which most of high-Tc superconductors has [6].

Specimens for HR-HVEM are in a form of crystal fragment. At the edge of specimens, therefore, we can sometimes observe the phenomena, which are characteristic of the reaction at the surface. We have succeeded in observing the chemical reaction for ReO_3 crystal and elucidating its mechanism [7].

Ultra-high resolving power of the present HR-HVEM enabled us to detect point defects like vacancies, which relate to the non-stoichiometry in crystals. Besides, the radiation by highly energetic incident electrons caused to generate vacancies in some inorganic compounds [8].

Many high-Tc superconductors have modulated structures, which are difficult to analyze by conventional X-ray diffraction method since they have large size of unit cell and complicated array of atoms. The present HR-HVEM was successfully utilized to this problem [6]. Lattice defects and grain boundaries were analyzed by the HR-HVEM and the origin of the flux pinning, being important to increase the critical current density of superconductors, was made clear [9,10]. The structural information obtained was effectively used to interpret the motion of magnetic flux observed by means of cryo-Lorentz EM [11].

2. Searching for new materials by means of HR-HVEM

HR-HVEM can be used especially when materials are very small, structures are rather complicated, and/or shapes are unusual beyond our imagination. In these cases there arise big chances to find new materials.

2.1. Creation of ceramics-related quasicrystals

Quasicrystals so far found always consist of alloys. We wanted to find out ceramics-related quasicrystals. Ta and Te were contacted and heated. At the boundary two thin layers were created. One of them gave the diffraction pattern with twelve-fold symmetry. Detailed analysis by the HR-THVEM made it clear that this is a new quasicrystal, whose composition is $Ta_{62}Te_{38}$ [12].

2.2. Facilitation of the preparation method for super-hard, cubic BN

Cubic BN is very hard and used widely as a polishing material for steel products. Conventionally it is prepared by the phase transition from hexagonal BN under high pressure like 7GPa at high temperature like 1800℃, which are very severe to realize. We have ball-milled the starting hexagonal BN. According to HR-HVEM it was clear that lots of lattice defects were introduced by the milling. With the milled powders the phase transition to cubic BN became easy. We can understand the reason for this from the viewpoint of mechano-chemical effect [13].

2.3. Preparation of ultra-hard, cubic C_3N_4 nanoparicles by thermal plasma method

According to the computer simulation, cubic C_3N_4 is expected to be harder than diamond. However any trial so far have not succeeded in preparing it under high pressure at high temperature. We have tried its preparation by using a plasma method, i.e. carbon particles including a slight amount of nitrogen was inserted into the atmosphere of induction thermal plasma at more than 2000℃. Nano-scale particles were created on the carbon particles with the composition of about C_3N_4. The crystal structure is cubic, but the lattice parameter is slightly (8%) larger than that expected [14].

2.4. Preparation of carbon nanofilms

Graphite was oxidized by strong chemical reagents. In the solution it was purified without being dried. In this process the very thin carbon films (carbon nanofilms) were produced. They were analyzed by HR-HVEM. It was clarified that the thickness is less than nm and the crystal structure consists of graphenes stacking in the sequence of ..AA.. . It was furthermore found that some fraction of them are graphene itsself [15].

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