Present research at Toyota riken

Development of Atomic-resolution Holography Microscope Compact DELMA for Direct 3D Viewing Atomic Arrangement around Isolated Atoms in Nano-area

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1. Atomic-resolution holography

The functionality of many functional materials can be improved by adding small amount of additives. A typical example is a dopant in Si. Si crystal is widely used for semiconductor electronic devices to realize computer or mobile phones. However Si itself cannot work as a semiconductor-device materials. It is necessary to add dopants such as boron or arsenic to realize p-type or n-type semiconductors. Simple injection of dopant atom is, however, not enough to make the atom active for the desired function. The doped atom is expected to work as a dopant only when it substitute a bulk Si atom. If the doped atom is located at an interstitial position, the valence of the doped atom is different from the substituted atom, and carrier cannot be produced. Hence the local structure around dopant is a key for the atom to work as a dopant. Here this local structure around dopant is called "active-site", which is a keyword governing functions in all inorganic-, organic- and bio- functional materials. The 3D atomic structures around the active-site atoms, however, cannot be analyzed by a standard structure analysis methods of x-ray or electron diffraction because this kind of active-site has no translational symmetry.

Recently several techniques have been developed to investigate the 3D atomic arrangement of active-site which has no translational symmetry. Typical methods are atomic-resolution holographies [1, 2] firstly suggested by Szöke [3]. Atomic-resolution holographies includes “photoelectron holography [4-7]”, “X-ray fluorescence holography [8-10]”, and “neutron holography [11, 12]”. In these holographies, the angular distribution of photoelectrons, fluorescent x-rays, and neutrons are measured, which includes the interference between the direct wave from (/or to) the emitter atom and the scattered waves from surrounding atoms. Because the phase difference information between the direct wave and the scattered waves are recorded, the angular distribution pattern is considered as a hologram [3], and the real-space atomic arrangement is easily calculated directly. Recently the accuracy of reconstructed atomic positions improved dramatically by the development of new analysis code [13-15] and a sensitive analyzers and detectors. A holography to study surface and interface atomic structure was also developed as “CTR holography [16]”. A new technique of “stereography of atomic arrangement” [17] has also been developed to study the local non-periodic atomic structure, which is not a holography but more direct method of stereo-viewing of 3D atomic structure around specific atoms directly with our eyes without any calculation.

All these techniques have been developed in Japan and received renewed attention recently. Hence a new project "3D Active-Site Science" of JSPS Grant-in-Aid for Scientific Research on Innovative Areas [18] has been pursued for five years. A lot of results from electronic-device-materials to bio-materials have been obtained throughout this project [19]. Some of the revealed structures are very strange and unexpected. Theoretical works confirmed the function of these strange local structure and even more predict a new local structure of effective functions. Hence a new field of *local functional structure science* is growing. Japanese [20] and English [21] text books have already been published. Effective and easy-to-use analysis software has been opened to public [22], which was downloaded about 1800 times. New notation system of local active-site has been proposed [2].

As written above atomic-resolution holography is very powerful to study local non-periodic atoms in functional materials. However, holographic measurement requires synchrotron radiation so far, and analysis on an industrial site has been impossible. In order to make use of this technique in society widely, it is necessary to develop an instrument that can measure atomic resolution holography in a laboratory. In

this study, we develop an atomic-resolution holography microscope, Compact DELMA, which aims to make it possible to view the local atomic arrangement around isolated atoms stereoscopically anywhere. The analysis of isolated atoms in micro-samples and micro-areas smaller than 1μm will become possible for the first time in the world, which will greatly contribute to the elucidation of atomic-level functions in the functional materials and nano-device industries.

2． Efficient energy analyzer

In order to take hologram effectively, the energy analyzer should have high energy-resolution with wide acceptance angle. The most common concentric hemispherical analyzer (CHA) has high-energy-resolution capabilities, but it is not efficient for angular distribution measurement because its acceptance angle is limited to ±15°×±0.5° typically, which is about 1/3000 of 2π str. It is necessary to take holograms in a wide solid angles of nearly 2π sr. Hence it takes more than several days to take one holograms using CHA. Hence a display-type analyzer with a wide acceptance angle nearly 1π str is necessary for holography measurement.

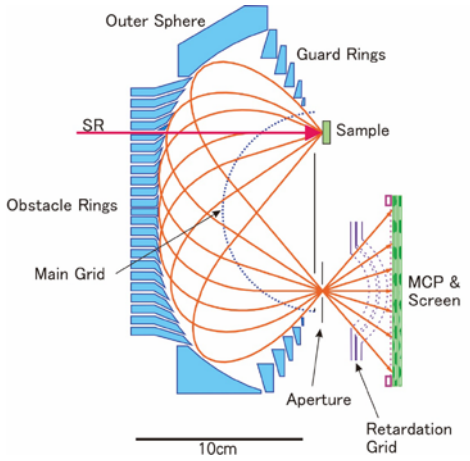

Fig. 1 DIANA [10, 11]

Several wide-angle display-type electron analyzers have been developed so far. An ellipsoidal mirror display analyzer was developed by Eastman et al. in 1980 [23], which can display ±43° cone (1.8 sr ≈ 0.3π sr) at once. It has a demerit that the pattern obtained is distorted. A display-type spherical mirror analyzer (DIANA) (Fig. 1) was developed by Daimon in 1988 [24], which can display ±60° cone (3.4 sr ≈ 1π sr) at once. It has a merit that the pattern obtained is not distorted. The energy resolution of DIANA is about 1%, which is not enough to measure chemical-shift-resolved hologram. To achieve high energy resolution a display-type ellipsoidal mesh analyzer (DELMA) (Fig. 2) was developed [25-29]. DELMA has microscope function with high energy resolution in addition to the feature of DIANA. DELMA consists of a wide-acceptance-angle electrostatic lens (WAAEL) [30-34], a transfer lens system, and CHA (VG Scienta R4000). WAAEL can accept wide angles of ±50° cone with reducing spherical aberrations to almost zero. This DELMA system can measure high-energy-resolution wide range 2D angular distribution by a deflector-scanning method. Here the ±50° cone 2D angular distribution formed at the detector plane of DELMA, which is the input plane of the CHA, is scanned using electrostatic deflectors, and many 1D (±12.5°×±0.5°) patterns obtained by the CHA are combined to construct the 2D pattern. These slices then can be combined to reconstruct the 2D real- or k-space images of the sample. Although, the DELMA solved DIANA's low-energy-resolution problem, but not used widely due to its complicated structure, large size, and relative high cost.

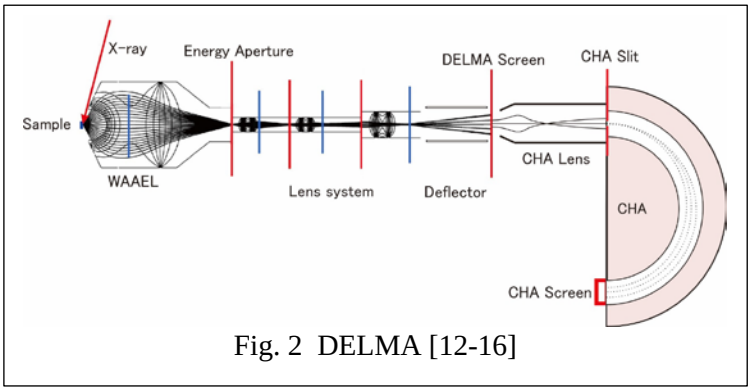

Fig. 2 DELMA [12-16]

Another approach is to use a PEEM technique [35], where a high accelerating voltage around 20 kV is applied between the sample and an objective lens. A very wide acceptance angle of almost ± 90° cone (2π sr) is achieved for photoelectrons of several tens eV. However, the acceptance angle rapidly decreases with increasing kinetic energy, and the angular range is not enough to study photoelectron holography at the

suitable kinetic energy of several hundreds eV. Recently another type of retarding-field analyzer (RFA) was developed [36]. RFA has wide acceptance angle of ±50° cone, and high energy resolution, but works well only at low binding energy photoelectrons.

In summary of this chapter, there is no ideal analyzer for atomic-resolution holography right now. Hence the purpose of research in Toyota Riken is to construct an ideal analyzer to take holograms, which has a capability of high energy-resolution and wide acceptance angle simultaneously.

3. VD-WAAEL Analyzer

The idea of the ideal analyzer (we call it Compact DELMA here) was reported in Ref. [37]. This analyzer is based on the technique of DELMA but is fundamentally different in the objective lens design. In DELMA, a wide-acceptance-angle electrostatic lens (WAAEL) of einzel type was used. This means that electrons leave the lens with the same kinetic energies as those at its entrance. As a result, for electrons with kinetic energy of E_k = 1 keV, high voltages up to around 5 kV should be applied to the lens after the objective lens to focus the electrons. The applied voltages linearly increase with the electron kinetic energy. This limits the kinetic energy range where DELMA can be used. A variable-deceleration-ratio wide-acceptance-angle electrostatic lens (VD-WAAEL) was proposed in Ref. [37]. VD-WAAEL is an improvement of deceleration-type WAAEL in Ref. [38], which cannot change the deceleration ratio. VD-WAAEL system can change the deceleration ratio in a wide range without changing the electron focusing at the exit of the lens. This feature is necessary in the measurement at high kinetic energies. When we decelerate the electron kinetic energy, the energy resolution become high and the voltages applied to the lens decreases. The acceptance angle of VD-WAAEL is the same as that of WAAEL of ± 50° cone.

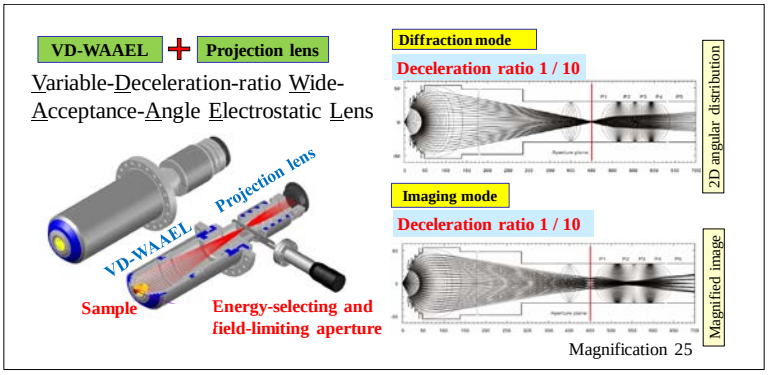

Fig. 3 VD-WAAEL analyzer [39]

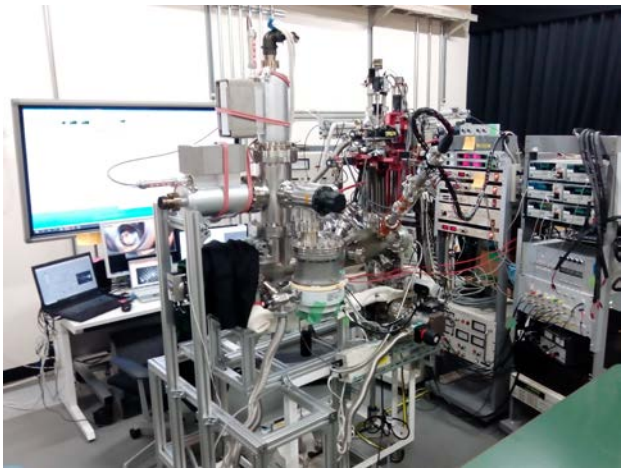
Fig. 4 Instrument of VD-WAAEL Analyzer.

The simplest analyzer using VD-WAAEL is a "VD-WAAEL analyzer" which is just a combination of VD-WAAEL, projection lens and a screen, along with an energy-selecting aperture [39] as shown in Fig. 3. VD-WAAEL analyzer has both diffraction and imaging modes, and it can switch these modes just by changing voltages of lenses. The imaging mode is used to display a magnified image of the sample on a screen, and it is useful to see the sample surface. The test of VD-WAAEL analyzer was done in Nara Institute of Science and Technology (NAIST). The angular distribution pattern, energy resolution, and magnified image

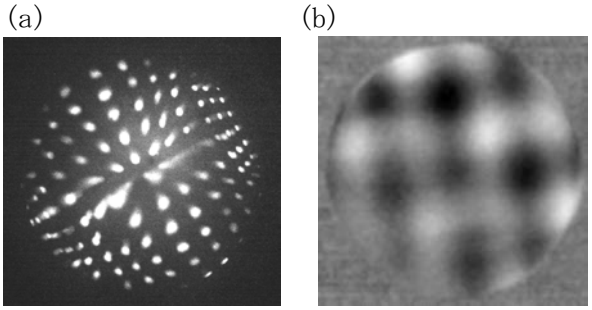

Fig. 5 (a) Angular distribution pattern and (b) magnified image of mesh sample taken at Toyota Riken.

were obtained successfully [39].

The instrument of VD-WAAEL analyzer was moved from NAIST to Toyota Riken and many improvement was done as shown in Fig. 4. The electron gun was remodeled to produce fine electron beam. The reproducibility of the angular distribution pattern and magnified image were confirmed successfully as shown in Fig. 5.

This simple analyzer has good energy resolution only at large angles more than 20°, because the principle of energy selection is focus-defocus type. Even though large angular range can be used to take hologram, the central area of 0° – 20° cannot be used. Hence we are developing the final analyzer Compact-DELMA.

4. Atomic-resolution Holography Microscope Compact DELMA

A diagram of Compact DELMA system is shown in Fig. 6. As seen in Fig. 6 an energy analyzer was inserted between VD-WAAEL and projection lens in VD-WAAEL analyzer. A high-energy-resolved electron hologram will be displayed on the screen of Compact DELMA in a wide angular range of ± 50° cone.

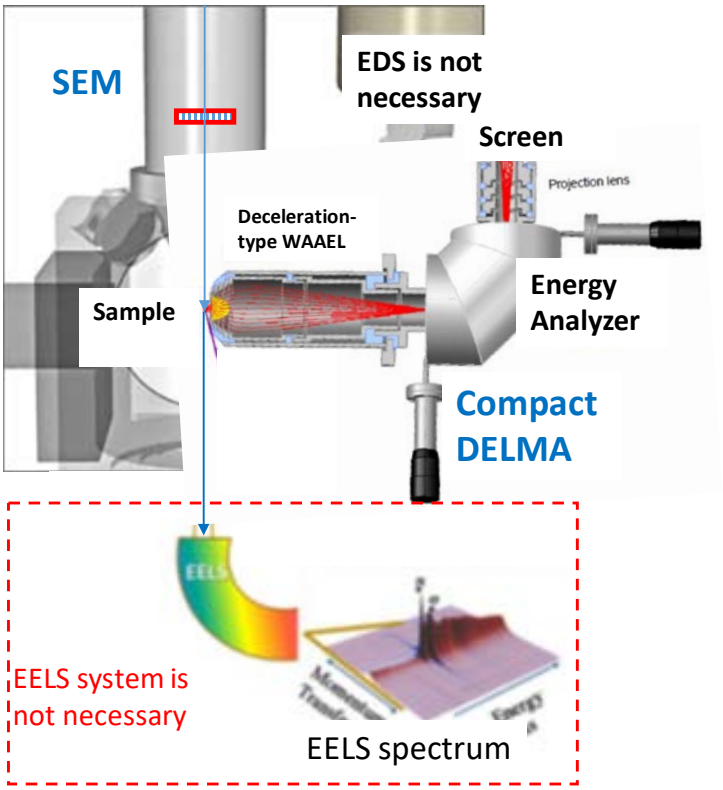

Fig. 6 Compact DELMA system

Because Compact DELMA is to be used in a laboratory without synchrotron radiation, the excitation source is an electron beam. Hence a combination of Compact DELMA and SEM (Scanning Electron Microscope) as shown in Fig. 6 is preferable. The hologram can be measured using Auger electrons or energy-loss electrons emitted from the nano-area irradiated by SEM electron beam. Hence nano-sized electron beam is important to take hologram from nano-area. A small SEM from APCO Ltd. has been installed in this system. When the size of electron beam is small, the energy resolution becomes high. The sample surface is characterized by SEM image. Hence a high-energy-resolved hologram of local isolated atom from selected nano-area can be obtained using this Compact DELMA system.

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