

Grazing Incidence Resonant X-ray Scattering for Self-assembled III-V Quantum Dots

Nano-sized objects – quantum dots and wires – exhibit unique physical properties different from their macroscopic counterparts due to quantum confinement of electrons and holes. This adds new functionality in the design of future electronic and optoelectronic devices. A common method to fabricate semiconductor quantum dots is self-assembled growth of strain-induced heteroepitaxial islands. The dots formed before the critical thickness for plastic relaxation being reached are dislocation free (coherent) and often exhibit a preferred shape with narrow size distribution. Because the atomic structure and compositional profiles play the key roles in determining the electronic structure of these dots, the knowledge of their formation mechanism is critical in order to control shapes, strain, and size distribution. Therefore, characterization techniques for structural and compositional parameters is of particular importance. It provides not only the necessary information to verify various formation models but also the input data for the understanding of optoelectronic properties.

It is well known that X-ray scattering can offer an ensemble average of the structural information of materials, both in internal atomic structure and inter-island spatial correlation. Moreover, X-ray scattering can also provide accurate chemical information, which can hardly be obtained by other techniques. In many early works, experimentally obtained lattice parameters are used to calculate the composition on the assumption of the validity of the Vegard's law, which states the lattice parameter of an alloy is a linear combination of that of the consisting components weighted by their contents, e.g. $a_{\text{In}_x\text{Ga}_{1-x}\text{As}} = x \cdot a_{\text{InAs}} + (1-x) \cdot a_{\text{GaAs}}$. However, the Vegard's law is known for bulk materials but may not be applicable to quantum materials because the lattice relaxation due to their mesoscopic size and hetero-interfacial lattice mismatch. Therefore, a strain independent method has to be employed to determine the composition of quantum materials. In this article, we address the capability of X-ray scattering in resolving the composition distribution of nanomaterials. We will demonstrate that in addition to the strain field, the compositional profile of nano-sized InGaAs quantum dots can be determined with high resolution by x-ray scattering.

The InGaAs quantum dots studied were prepared by solid-source molecular beam epitaxy on a GaAs(001) substrate with misorientation less than 0.02° . $\text{In}_x\text{Ga}_{1-x}\text{As}$ with nominal composition of $x = 0.5$ were then deposited at 520°C with a deposition rate of 0.5 ML/s. Under this condition, three-dimensional islands were formed after 5 ML of deposition, indicated by the appearance of a spotty-

like reflection high-energy electron diffraction (RHEED) pattern. An atomic force microscopy image of the sample surface is illustrated in Fig. 1. Islands with lateral size of a few tens of nanometer are distributed uniformly on the surface. The number density of dots, estimated from the AFM image, is $5 \times 10^{10} \text{ cm}^{-2}$. Grazing incidence x-ray scattering measurements were conducted at the wiggler beamline BL17B1 at Taiwan Light Source and the Taiwan contract beamline BL12B1 at SPring-8.

The application of the reciprocal space map method to determine the structure of semiconductor quantum dots was first demonstrated by I. Kegel *et al.* in 1999. They studied uncapped InAs quantum dots grown on GaAs(001). The basic idea there is the lattice of coherent quantum dots is in registry

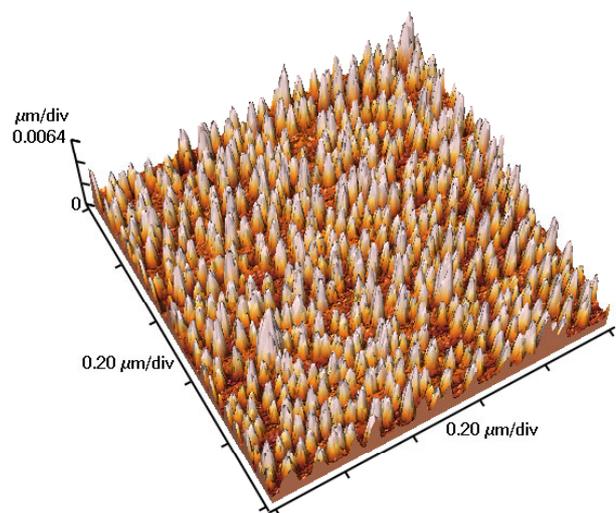


Fig. 1: An AFM micrograph of the uncapped $\text{In}_x\text{Ga}_{(1-x)}\text{As}$ quantum dots grown on GaAs(001) surface.

with that of the substrate and it varies monotonically from the bottom to the top. Therefore, quantum dots can be divided into regions with constant lateral lattice parameter, the iso-strain region. Because of the absence of the periodicity in lattice along the growth direction, only the surface Bragg peaks (HK0), exist for each iso-strain region. Furthermore, the surface diffraction (HK0) of iso-strain regions with larger lateral lattice parameter will center at smaller radial scattering vector, q_r , along the [HK0] direction in the reciprocal space and vice versa. Therefore, by detailed analysis of the intensity distribution in the corresponding region in reciprocal space, we can determine the lateral dimensions, height above the surface of each iso-strain region and thus reconstruct the size, shape and strain field of the quantum dots.

The concept that the structure factor is a simple linear combination of atomic scattering factors and molar percentage of consisting elements is employed in uncovering the compositional profile. For the ternary III-V semiconductor $\text{In}_x\text{Ga}_{(1-x)}\text{As}$ with the zinc-blende structure, its structure factor of the (HKL) Bragg peak, F^{HKL} , is expressed as

$$F^{HKL} = \left[x f_{\text{In}} + (1-x) f_{\text{Ga}} + f_{\text{As}} e^{i\frac{\pi}{2}(H+K+L)} \right] \cdot \left[1 + e^{i\pi(H+K)} + e^{i\pi(K+L)} + e^{i\pi(L+H)} \right] \quad (1)$$

where f 's denote the atomic scattering factors and x represents In concentration. In concentration x can be determined experimentally by comparing the intensity ratio between a strong and a weak diffraction, e.g. the (400) and the (200) Bragg peaks associated with the same iso-strain region, with the calculated value based on Eq. 1. The information so obtained together with the strain field determined from the reciprocal space map method allow us to rebuild the compositional profile of the dots. Nevertheless, the accuracy of the intensity ratio is sensitive to the experimental details. For example, small deviation in incident angles of the two diffractions may cause significant difference in results. Moreover, when the spatial distribution of the quantum dots exhibits ordered arrangement, then significant intensity modulation introduced by inter-dot correlation will appear near the substrate surface Bragg peaks. The presence of these additional interference peaks hinders the applicability of this method.

It is well known that atomic scattering factor is a slow varying function of photon energy except near the absorption edge of an element, the so-

called anomalous dispersion. To take the energy dependent variation into account, the atomic scattering factor is often described by three terms:

$$f(q, E) = f^0(q) + f'(E) + if''(E) \quad (2)$$

where f^0 is the Thomson scattering factor. The value of f^0 is close to the atomic number of the element when the scattering vector q is small. f' and f'' are the real and imaginary part of the dispersion corrections, respectively; they change drastically only when the energy of probing X-ray is close to the absorption edges of the element. Accordingly, diffraction intensity will exhibit a pronounced fluctuation as photon energy is scanned across the absorption edge of any consisting elements and the spectrum profile is sensitive to the chemical composition. The change in the profile of energy spectra is particularly enhanced when a proper diffraction and a proper absorption edge are chosen. Figure 2a illustrates the simulated spectra of the (200) diffraction of $\text{In}_x\text{Ga}_{(1-x)}\text{As}$ near the Ga K -absorption edge, 10.367 keV, where the theoretic anomalous scattering factors by S. Sasaki are adapted. The fact that a small change in x leads to a significant change in spectrum profile manifests the high sensitivity to compositional variation. As a comparison, the spectra of the (400) diffraction are also displayed in Fig. 2(b) and no obvious difference in shape is observed.

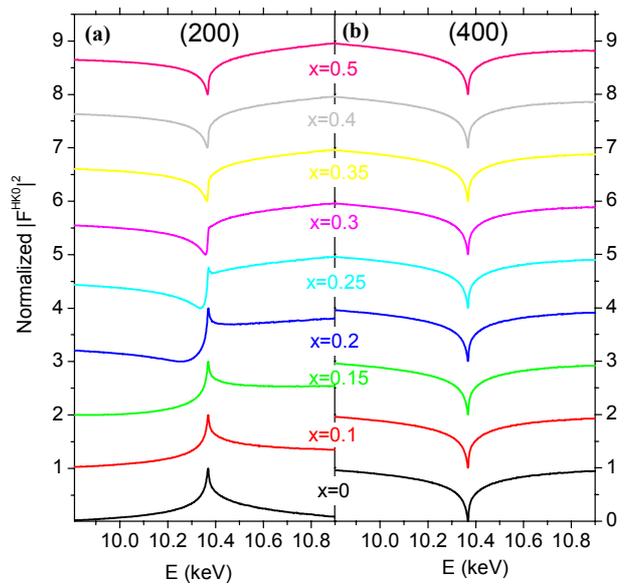


Fig. 2: (a) Calculated $|F_{\text{In}_x\text{Ga}_{(1-x)}\text{As}}^{200}|^2$ as a function of In concentration x . Spectra profile is highly sensitive to x , in particular in the range $0.1 < x < 0.4$, and can be used to determine x . As a comparison, calculated $|F_{\text{In}_x\text{Ga}_{(1-x)}\text{As}}^{400}|^2$ are also displayed in (b), which show no difference in the profile shape.

Near the GaAs (200) diffraction, energy scans across Ga K absorption edge at q_r 's corresponding to different iso-strain regions are conducted. The obtained spectra are depicted by filled circles in Fig. 3 with the corresponding q_r 's marked by the arrows of the same color in the radial scan shown in the inset. The manifest difference in profiles elucidates that the composition of dots is far from being uniform. Pronounced intensity modulation above the absorption edge is attributed to the x-ray absorption near-edge structure, XANES, which is related to the electronic state of Ga atoms and the local structure surrounding it. The f'' of Ga is obtained experimentally by measuring the absorption spectrum of the sample and f' is subsequently calculated from the measured f'' according to the Kramers-Kronig transformation. To further take the contribution from the neighboring iso-strain regions into account, the square of the structure factor is convoluted with a gaussian composition distribution with an average In concentration \bar{x} and width Δx . An additional energy dependent absorption correction term A is also included in the model calculation.

$$I(E) \propto A(E) \cdot \int |F(q, E, x)|^2 \exp[-(x - \bar{x})^2 / \Delta x^2] dx \quad (3)$$

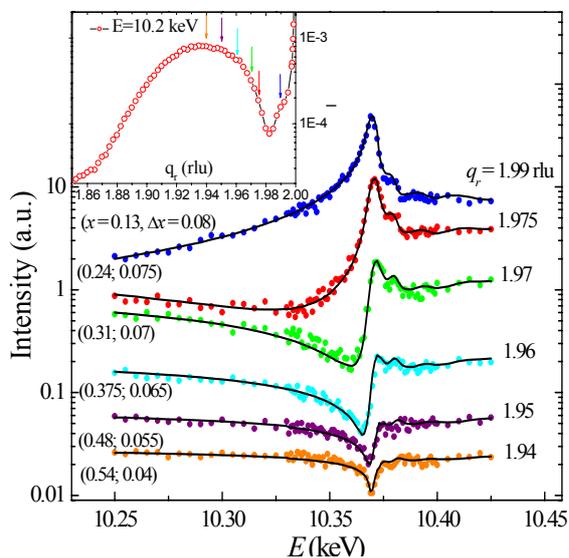


Fig. 3: Filled circles depict the measured energy spectra collected at various q_r 's near the GaAs (200) surface Bragg peak as marked by the arrows of the same colors on the radial scan shown in inset. The solid curves are the best-fit results obtained by convoluting $|F_{\text{In,Ga}_{1-x}\text{As}}^{200}|^2$ with a gaussian composition distribution. The average x and the width Δx of each gaussian distribution are marked on the left of the corresponding curve.

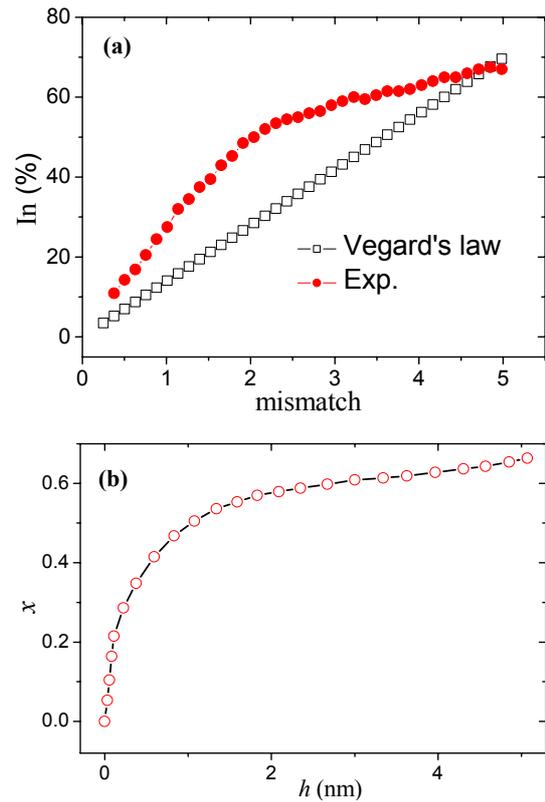


Fig. 4: (a) Measured In concentration (filled circles) as a function of lattice mismatch with GaAs substrate. The In concentrations calculated from the lattice mismatch based on the Vegard's law (open squares) are also displayed for comparison. (b). In concentration as a function of height h above the sample surface.

The calculated intensities are displayed by the solid curves with the best-fit value of \bar{x} and Δx marked on the left of corresponding curve. The obtained In concentration x (filled circle) as a function of lattice mismatch with GaAs is plotted in Fig. 4(a), which reveals that In concentration increases monotonically with lattice mismatch. As a comparison, In concentration calculated from the lattice mismatch according to the Vegard's law is also shown by open squares in Fig. 4(a). Evidently, the In distribution within the quantum dots does not obey the Vegard's law. With the concentration taken into account, most part of the dot interior is compressively stressed.

From the results of the reciprocal space map, which is not shown here, we learned that the lattice mismatch of the dots with respect to the GaAs substrate also increases monotonically from the bottom to the top of the dots. Combining both results, we plot In concentration x as a function of height h above sample surface in Fig. 4(b). Again, x grows monotonically with h but it increases rapidly within the bottom 1 nm, where it reaches the

nominal 50%. Above 1 nm, x slowly rises from 50% to its maximal value ~67% at the top. It is also noteworthy that the maximal In concentration of the dots ~70% is significantly higher than the nominal composition 50%. This is attributed to the In surface segregation which has been reported in similar systems. Moreover, the interfacial diffusion of Ga/In at the dot/substrate interface is another cause of In depletion at the bottom of the dots.

In summary, we have demonstrated that the combination of reciprocal space map and the resonant X-ray scattering is a powerful technique to resolve the compositional distribution of nanomaterials. In particular, the choice of weak diffraction together with the proper absorption edge can greatly raise the accuracy and resolution in composition determination. In the case of $\text{In}_x\text{Ga}_{(1-x)}\text{As}$, the combination of the (200) diffraction and Ga K -edge is an ideal choice. Under this circumstance, this method is most sensitive to In concentration of 5-50%. The highly sensitive range can be further extended downward by using As K -edge and upward by using (600) diffraction. Furthermore, it is important to note the profile of energy spectrum is what bears the information of composition in this method. Therefore, for the systems with strong spatial correlation, such as regularly arranged quantum dots and wires, the intense lattice-independent intensity modulation near the Bragg peaks hinders the application of those methods which rely on the intensity ratio of diffractions. Nanomaterials with high spatial ordering are systems where the advantage of this method can be fully demonstrated.

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BEAMLINES

SP12B Biostructure and Materials X-ray Research beamline
17B W20 X-ray Scattering beamline

EXPERIMENTAL STATION

X-ray Scattering end station

AUTHORS

C.-H. Hsu, Y. Stetsko, M.-T. Tang, H.-Y. Lee, C.-M. Huang, and K. S. Liang
National Synchrotron Radiation Research Center, Hsinchu, Taiwan

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- Y. P. Stetsko, C.-H. Hsu, M.-T. Tang, Y.-R. Lee, U.-S. Jeng, and K. S. Liang, (2004), submitted.
- 徐嘉鴻, "半導體量子點的結構研究", *物理雙月刊* **26**, 395 (2004).

CONTACT E-MAIL

chsu@nsrrc.org.tw