Characterization of quasicrystalline Al-Cu-Fe nanoclusters as catalysts for the synthesis of carbon nanotubes

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Abstract. Quasicrystalline (QC) Al-Cu-Fe nanoclusters as catalysts for the synthesis of carbon nanotubes (CNTs) were characterized in this study. It was shown in previous work that armchair-type CNTs are preferentially synthesized by using Al-Cu-Fe ultrathin films as catalysts in catalytic-chemical vapour deposition. We postulated a plausible mechanism that facets of QC nanoclusters with fivefold symmetry play an important role in the nucleation of a CNT cap with specific six-pentagon-configuration, which gives rise to the selective synthesis of armchair-type CNTs. To verify this hypothesis, the morphology and structure of Al-Cu-Fe nanoclusters were investigated by using transmission electron microscopy and electron diffraction (ED) as well as X-ray diffraction. As a result, it was found that the morphology of their nanoclusters is generally faceted-polyhedra, and the average diameter is ~4 nm, ranging from 1 to 10 nm, which indicates to correlate with the diameter of CNTs synthesized by using these nanoclusters as catalysts. Their ED patterns could be attributed to an icosahedral (i) Al-Cu-Fe phase. It was also found that multi-walled CNTs are synthesized successfully by using i-Al-Cu-Fe, i-Al-Pd-Re, and decagonal-Al-Ni-Co bulk-alloy systems as catalysts, respectively.

1. Introduction
Over the last decade, the synthesis of carbon nanotubes (CNTs), having suitable physical and chemical properties for industrial applications such as field emission cathodes in flat panel displays, has been developed towards the chirality-controlled synthesis [1]. In recent years, it has been reported that the morphology and structure of catalytic metal nanoclusters, for example, Fe-Co [2] and Co-Mo [3], as well as the synthetic conditions play an important role in determining both diameter $d_t$ and chirality $(n,m)$ of CNTs synthesized by catalytic-chemical vapor deposition (CVD) using a carbon source gas supply such as ethanol and CO. Based on the dissolution-diffusion-precipitation model [4] for the synthesis mechanism of CNTs, a hydrocarbon such as ethanol adsorbed on the catalytic cluster surface releases carbon upon decomposition, which dissolves and diffuses into the cluster. When a supersaturated state is reached, carbon precipitates in a crystalline tubular form. It is supposed that (i) the solid solubility of carbon into clusters is a dominant factor rather than chemical reaction on the cluster surface in the dissolution step, and (ii) the template effect of clusters is a dominant factor on the diameter and the tube chirality in the precipitation step.

As shown in previous work [5], we have studied quasicrystalline (QC) Al-Cu-Fe nanoclusters as catalysts for the chirality-selective synthesis of armchair-type, i.e., metallic, CNTs, since it is known that the chirality of CNTs depends on the configuration of six pentagons at the cap in the precipitation step, and an armchair tube is formed if the fullerene $C_{60}$, having a truncated-icosahedral structure, is
bisected normal to a fivefold axis [6]. As described previously [5], we postulated a mechanism of chirality-selectivity using QC nanoclusters as catalysts that a pentagon accompanied with five hexagons is epitaxially formed at the center of a hemi-fullerene cap of the CNT on a facet of icosahedral (i) nanoclusters with fivefold symmetry, followed by adding five pentagons and a cylinder of graphite, resulting in an armchair-type CNT due to the catalytic activity of i-nanoclusters.

In order to verify this hypothesis, first of all in this exploratory work, we focused on the geometric structure of the clusters, especially on the quasicrystallinity of Al-Cu-Fe nanoclusters. The morphology and structure of Al-Cu-Fe nanoclusters, which are formed by annealing at 723 K for 30 min in Ar ambient [5], were investigated by using transmission electron microscopy (TEM), electron diffraction (ED), and energy-dispersive X-ray spectrometry (EDS), compared with our conventional Al-Co two-layered films [7]. Since Co-based alloys are commonly used for catalysts in the catalytic CVD of CNTs using ethanol as a carbon feedstock [2,3,7-9], and also a few reports on chirality distributions using only Co-based alloys as catalysts are available so far [2,3].

Secondly, whether i-Al-Cu-Fe, i-Al-Pd-Re, and decagonal (d) Al-Ni-Co bulk-alloy systems [10], of which QC phases were confirmed by X-ray diffraction (XRD), have a similar catalytic-activity for the synthesis of CNTs or not were investigated by using scanning electron microscopy (SEM) as well as TEM. Finally, at the current state, a most probable mechanism of chirarity-selectivity by using QC nanoclusters as catalysts is described in this article. However, further work is needed to clarify the catalytic effect of electronic structure of the cluster surface on the synthesis of CNTs.

2. Experimental Details
First, Al (2.1 nm)/Cu (0.6 nm)/Fe (0.3 nm) three-layered films were deposited on rock-salt/SiO₂ (50 nm thick) substrates by sequential electron-beam evaporation, followed by annealing at 723 K for 30 min in Ar ambient in a CVD reactor to form nanoclusters having an icosahedral phase, i.e., i-Al₆₂Cu₂₅.₅Fe₁₂.₅ [11-13], as described in detail previously [5]. Subsequently, these annealed Al-Cu-Fe ultrathin films were removed from the substrates, and were put them on TEM grids. Then the morphology of Al-Cu-Fe nanoclusters was observed by TEM, and also both electron diffraction patterns and EDS spectra were obtained from these nanoclusters.

Secondly, in order to compare with the results on Al/Cu/Fe three-layered films, the procedures above-mentioned were performed on conventional Al (2 nm)/Co (1 nm) two-layered films, where the annealing were executed at 973 K for two hours in air ambient [5, 7].

Thirdly, in order to investigate the catalytic activity of QC bulk-alloys, both i-Al₆₂.₅Cu₂₅.₅Fe₁₃ and i-Al₇₀Pd₃₀Re₁₀ alloy pellets, and also a d-Al₇₀Ni₁₅Co₁₅ alloy pellet were prepared by furnace alloying and subsequent annealing, respectively. Then XRD with Cu K辐射 was used for evaluation of the quasicrystallinity of these alloy pellets. Both i-QC alloy pellets were crushed by grinding with an agate pestle in a mortar, and then these i-QC alloy suspensions dispersed by ultrasonication in ethanol were deposited and dried on silicon (100) wafer substrates (10 mm squares and 0.5 mm thick), respectively. These samples were annealed at 723 K for 30 min in Ar ambient in a CVD reactor, followed by synthesizing CNTs at 973 K for 5 min by ethanol catalytic-CVD, i.e., under the same conditions as described previously [5]. Subsequently, as-prepared CNTs were observed by using SEM (S-4000, Hitachi) and TEM (H-800, Hitachi) to characterize the morphology and structure of CNTs.

3. Results and discussion
3.1. The morphology and structure of Al-Cu-Fe nanoclusters
Figures 1(a) and 1(b) show a TEM image and an ED pattern of Al-Cu-Fe nanoclusters, respectively, and the inset in figure 1(a) shows a TEM image of CNTs synthesized by catalytic-CVD using these nanoclusters as catalysts. Figure 2 also shows an EDS spectrum of Al-Cu-Fe nanoclusters. From TEM observation (figure 1(a)), the morphology of most nanoclusters is so-called faceted-polyhedra [14], and the average diameter of nanoclusters, dₙ, is about 4.5 nm, ranging from 1 nm to 10 nm, which indicates that dₙ correlates to the average diameter of CNTs, dₙ ≈ 3 nm as shown in the inset. From
Figure 1. (a) TEM image and (b) ED pattern of Al-Cu-Fe nanoclusters. The inset in (a) shows a TEM image of CNTs synthesized by catalytic-CVD using Al-Cu-Fe nanoclusters as catalysts.

Figure 2. EDS spectrum of Al-Cu-Fe nanoclusters.

Figure 3. XRD pattern of an i-Al-Cu-Fe alloy pellet.

an EDS spectrum (figure 2), as expected, nanoclusters consist of Al, Cu and Fe, while a carbon peak could originate from a TEM grid used here.

Debye rings obtained in an ED pattern (figure 1(b)) give the values of interplanar spacings, \( d = 0.248, 0.201, 0.175, 0.146, 0.124, \) and \( 0.106 \) nm, respectively, from inner- to outer-ring order. According to the indexing of the XRD pattern obtained from the \( i\text{-Al}_{62.5}\text{Cu}_{24.5}\text{Fe}_{13} \) alloy pellet as shown in figure 3, where the \((N, M)\) indexing scheme of Cahn et al. \[15\] is used for a QC phase, these Debye rings could be attributed to the indices of \((14, 21), (20, 32), (27, 43), (38, 61), (52, 84) \) and \((72, 116)\), respectively, in the above order. From these indices, it indicates that the structure of Al-Cu-Fe nanoclusters is confirmed to be of face-centered-icosahedral phase \[15\].

It is well-known that the formation route of the QC nanoclusters considerably affects the morphology and structure of nanoclusters. In this study, in the case of Al/Cu/Fe sequential deposition, isolated faceted-polyhedral, presumably icosahedral, nanoclusters are formed by an appropriate heat-treatment as shown in figure 1(a), and these nanoclusters have a higher catalytic activity rather than in the case of Al/Fe/Cu sequence (not shown here). It suggests that further study of QC nanoclusters with
more suitable morphology and structure as catalysts is needed for a specific \((n, m)\) selective-synthesis of CNTs in catalytic-CVD.

3.2. The morphology and structure of conventional Al-Co nanoclusters

Figures 4(a) and 4(b) show a TEM image and an ED pattern of conventional Al-Co nanoclusters, respectively, and the inset in figure 4(a) shows also a TEM image of CNTs synthesized by catalytic-CVD using Al-Co nanoclusters as catalysts, for comparison with the above-mentioned QC Al-Cu-Fe nanoclusters. From TEM observation (figure 4(a)), the morphology of Al-Co nanoclusters is slightly different spherical-, including irregular-shaped, polyhedra from the Al-Cu-Fe nanoclusters, while the average diameter of nanoclusters has a quite similarity to the Al-Cu-Fe nanoclusters. Based on the chirality assignment by radial-breathing mode Raman scattering, we obtained previously \([5]\) a different chirality distribution using Al-Co nanoclusters from that using \(i\)-Al-Cu-Fe nanoclusters.

Debye rings obtained in an ED pattern (figure 4(b)) give the values of interplanar spacings, \(d = 0.245, 0.209, 0.173, 0.142, 0.134, \text{ and } 0.123 \text{ nm, respectively, from inner- to outer-ring order. Based on the powder-diffraction database, Al-Co nanoclusters could be attributed to both AlCo}_2O_4 \text{ and } \bar{\text{t}}\text{-}Al_2O_3 \text{ mixed phases, which have a poor crystallinity according to halo-like rings.}

It is reported by Liu \textit{et al.} \([16]\) that \(\bar{\text{t}}\text{-}Al_2O_3\) particles less than 3 nm in diameter have a catalytic activity for the synthesis of CNTs, but their chirality distribution of CNTs is different from our results of both Al-Cu-Fe and Al-Co nanoclusters, which were described previously \([5]\). It was also shown in previous work \([5]\) that CNTs using Al-Co nanoclusters have a broader chirality distribution rather than those using QC Al-Cu-Fe nanoclusters, and the relative abundance of armchair-type CNTs is \(\sim 31\%\) for the former, whereas that is \(\sim 55\%\) for the latter. It might indicate that the morphology of Al-Co nanoclusters is less preferred to be faceted-polyhedra \([17]\), for example, icosahedra, rather than \(i\)-Al-Cu-Fe nanoclusters.

3.3. Catalytic activity of quasicrystalline bulk-alloys

Moreover, we have also investigated whether or not CNTs are synthesized by catalytic-CVD using QC bulk-alloys as catalysts. Figures 5(a), 5(b) and 5(c) show SEM images of CNTs synthesized by using (a) \(i\)-Al-Cu-Fe, (b) \(i\)-Al-Pd-Re alloy powders, and by using (c) a \(d\)-Al-Ni-Co alloy pellet as catalysts, respectively. The inset in figure 5(c) shows, as an example, a TEM image of CNTs synthesized by using \(d\)-Al-Ni-Co alloy pellet as catalysts. From these results, it indicates that multi-walled CNTs (MWNTs) are synthesized successfully by using \(i\)-Al-Cu-Fe, \(i\)-Al-Pd-Re, and \(d\)-Al-Ni-Co alloys, respectively, where their diameters, \(d_o\), ranging from 10 nm to 30 nm, are considerably larger than \(i\)-
Al-Cu-Fe nanoclusters formed from ultrathin films. It is well-known that the diameter of CNTs dominantly depend on that of clusters due to the template effect, and also the number of walls depends on the diameter of CNTs. Based on the energetics of nanotubes, it is suggested that a larger (>3 nm) SWNT tends to collapse unless it is surrounded by neighbouring tubes, for example, as in a MWNT due to surface strain energy.

In the case of \(\text{i-Al-Cu-Fe}\) bulk system, we found the dark precipitates inside the CNTs to be Al-Cu-Fe compounds by means of energy-dispersive X-ray spectra in the TEM images (not shown here). Also, in \(d\text{-Al-Ni-Co}\) bulk system, we obtained ED patterns of clusters inside the CNTs, which could be attributed to the structure of decagonal Al-Ni-Co (not shown here). It is suggested that absorption phenomenon of nonwetting clusters originates from the capillary action by the inner wall of CNTs [18]. According as the bright precipitates inside the nanotubes in SEM images, typically as shown in figure 5(b), are considered to be QC alloy clusters, the average diameter of CNTs, \(d_t \geq 30 \text{ nm}\), is also correlated with that of alloy clusters, \(d_c\). It implies that larger QC clusters also have a significant catalytic activity for the synthesis of MWNTs with larger diameters.

However, this is a preliminary result performed on typical three QC alloy systems under the same synthetic conditions. Further study is still required for finding a more suitable QC alloy system and appropriate synthetic conditions for each alloy system in the field of controlled-synthesis of CNTs.

3.4. Mechanism of chirality-selectivity using quasicrystalline nanoclusters

It is well-known that the fullerenes, typically \(C_{60}\) with \(~0.7 \text{ nm}\) in diameter, have a truncated icosahedral structure with fivefold axis, and also the QC clusters have building-blocks of multi-shell, hierarchical structures, so-called pseudo-Mackay clusters [19]. Therefore, we have hypothesized that a pentagonal-carbon ring is nucleated epitaxially on a facet of QC nanoclusters, subsequently a hemi-fullerene cap with fivefold symmetry is formed around the pentagon, and then an armchair-type nanotube is elongated by the catalytic reaction of the QC nanoclusters.

From a preliminary work [5], in which the considerable preference of armchair-type CNTs by using QC nanoclusters as catalysts is shown, it could indicate that the facets of QC nanoclusters with fivefold symmetry play an important role in the nucleation stage of a CNT cap with a specific six-pentagon-configuration, which gives rise to armchair-type CNTs having a, as an example, \((9, 9)\) chirality, \(d_t \geq 1.22 \text{ nm}\) in diameter, corresponding to the diameter of QC nanoclusters.

Based on these evidences obtained from both this study and the previous work, it indicates that the chirality-selectivity of QC nanoclusters originates from the faceted-polyhedral template effect and the
surface atomic structure with fivefold symmetry of the QC nanoclusters. That is, the cap structure of CNTs reflects a six-pentagon-configuration in the nucleation stage of CNT-apex due to the interaction between C $2sp^3$ orbitals of carbon chains and Al $3sp^m$ orbitals of QC surfaces. It is suggested that (9, 9) armchair-type CNTs are self-assembled on the facets of pseudo-Mackay icosahedral clusters.

The surface of QC nanoclusters is probably covered with ultrathin aluminium oxide layer. This might influence the synthesis of CNTs, probably the growth rate, the diameter, and the tube chirality. Liu et al. [16] indicated that alumina nanoparticles less than 3 nm in diameter, or Al thin film oxidized in air, have a significant catalytic activity, but give rise to a different chirality distribution from the QC Al-Cu-Fe nanoclusters, i.e., non-armchair type CNTs are preferably synthesized by using alumina nanoparticles. However, further work is needed to clarify the influence of oxidation in the near future.

4. Conclusions

Over the last decade, nanoclusters [17], quasicrystals [10, 12, 19], and CNTs [1, 6] are fascinating fields in nanoscience and nanotechnology. In this article, nanoclusters having QC structures were investigated in applications to the catalysis for chirality-selective synthesis of CNTs.

First, it was found that the morphology of QC Al-Cu-Fe nanoclusters, which is transformed from Al-Cu-Fe ultrathin films by annealing at 723 K for 30 min in Ar ambient, is in general faceted-polyhedra, and their average diameter $d_c$ is ~4 nm, ranging from 1 to 10 nm, which implies to correlate with the diameter distribution of CNTs synthesized using QC nanoclusters as catalysts. Secondly, their ED patterns could be attributed to a face-centered-icosahedral Al-Cu-Fe phase. It could indicate that the hypothesis mentioned previously [5] is verified from these evidences, that is, the facets of QC nanoclusters with fivefold symmetry play an important role in the nucleation stage of a hemi-fullerene cap with specific six-pentagon-configuration of an armchair-type CNT such as (9, 9) with $d_t$ $\approx$ 1.2 nm.

In addition, it was found that multi-walled CNTs are synthesized successfully by using both $i$-Al-Cu-Fe and $i$-Al-Pd-Re alloy powders, as well as by using a $d$-Al-Ni-Co alloy pellet as catalysts for catalytic-CVD using ethanol as a carbon source. It indicates that larger QC faceted-clusters have a significant catalytic activity for the synthesis of multi-walled CNTs with approximately the same diameter as that of QC clusters, $d_t$ $\approx$ 30 nm.

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