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# Observations on the growth of Al–Ni–Co decagonal thin films by atomic force microscopy and transmission electron microscopy

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**Abstract**

Thin films of Al–Ni–Co alloy were produced by vacuum deposition technique using a substrate material of amorphous carbon thin-foil. Attempts were made to obtain a homogeneous decagonal quasicrystalline film, where the preparation technique was based on the direct evaporation of pre-alloyed ingot of $Al_{72}Ni_{15}Co_{13}$ onto the heated substrates. In order to explore early stages of the decagonal film growth, the Al–Ni–Co films with different thicknesses ranging from 2 nm to 30 nm were deposited on either substrates heated at 500 °C or non-heated substrates. The film samples so obtained were examined mainly by atomic force microscopy in combination with transmission electron diffraction and imaging techniques. On the basis of these observations, deposition conditions necessary for the growth of decagonal phase in the resulting films as well as the growth mechanism of the decagonal film will be discussed.


*Keywords:* Quasicrystals; Thin films; Vapor deposition; Scanning and transmission electron microscopy; X-ray diffraction

## 1. Introduction

The first challenging issue on quasicrystals (QC) that has been most highlighted is about their structural property [1] which is best characterized by a new type of atomic order called *quasiperiodicity*. Meanwhile, an enormous amount of investigation has been made to explore any physical property different from those of crystalline and amorphous materials. Some of the unique properties of QCs discovered so far, such as low friction and non-stick character, attract many scientists' attention to efforts aiming at technical application, for instance, surface coatings or even some optical and electric devices [2–4]. In these proposed applications, one of the most crucial tasks in the works is the development of a thin film technology for these materials. According to previous work, however, the number of reports dealing with the production of homogeneous quasicrystalline films by means of vacuum deposition technique is surprisingly limited due to technical difficulty in controlling stoichiometric condition required for the growth of QCs.

In general, there are three different methods of depositing alloy films: simultaneous evaporation of the component metals, successive evaporation of the component metals followed by interdiffusion (through postdeposition annealing) and direct evaporation of the alloy [5]. In fact, the production of quasicrystalline films has been attempted by a number of different techniques based on either of these methods. Many of the successful attempts, especially for ternary QC films, were based on the former two methods [6–12]. Among many deposition techniques, sputtering or laser abration combined with high vacuum pumping system, each of which is capable of minimizing contamination and controlling appropriately the composition of a multicomponent alloy film, seems to be highly effective in producing homogeneous quasicrystalline films such as Al–Cu–Fe [6], Al–Pd–Mn [7,13], Al–Cu–Co [8] and Ti–Ni–Zr [10] alloys. With regard to Al–Ni–Co decagonal (d)-film [9], by contrast, there are almost no experimental data available and many fundamental questions still remain to be solved about details of the preparation technique, not to speak of the growth mechanism as well as microstructure

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of the film. Essentially, the microstructure of the film is determined by the nucleation and early stages of film growth. It is therefore of great importance that the initial stages of film growth are fully understood. This is clearly also the case with thin films of the Al–Ni–Co d-phase.

In this paper, we report on the film preparation of the Al–Ni–Co d-phase. Attempts were made to obtain a homogeneous quasicrystalline film by means of vacuum deposition technique, which is based on the third method of depositing alloy films addressed above, namely the direct evaporation of pre-alloyed ingot of $Al_{72}Ni_{15}Co_{13}$ using amorphous carbon thin-foils as a substrate material. The Al–Ni–Co films with different thicknesses ranging from 2 nm to 30 nm were deposited on either heated- or non-heated substrates in order to explore the nucleation and early stages of film growth. Attention has been focused on the description of the nucleation process of d-phase which occurs during the film growth.

## 2. Experimental

For the production of Al–Ni–Co films, we employed the direct evaporation method of pre-alloyed ingot of $Al_{72}Ni_{15}Co_{13}$ using a resistance-heated tungsten boat as an evaporation source, while an amorphous carbon (a-C) thin-foil with an electron transparency, which is supported by a molybdenum mesh with a diameter of 3 mm, was chosen as a substrate material. In Fig. 1, we show AFM and TEM images of the bare a-C thin-foil as received from a vendor, in both of which the substrate appears to be highly smooth and continuous. The use of the a-C thin-foil as substrate is advantageous in that the deposited film can be directly examined by transmission electron microscopy (TEM) technique without making further specimen preparation usually required for TEM, thereby avoiding any possibility of defect introduction during the TEM specimen preparation. The $Al_{72}Ni_{15}Co_{13}$ alloy was prepared from pure metals Al (99.999%), Ni (99.9%) and Co (99.90%) in an Ar atmosphere using an arc furnace. The mother alloy was subsequently crushed into fine powder using an agate mortar and many sets of powdered ingots of different weights were evaporated separately in a vacuum of about $10^{-3}$ Pa onto the a-C substrates heated at various test temperatures ranging from 20 °C to 500 °C. In this way, the Al–Ni–Co films of different thicknesses were obtained on the substrates, where the word *thickness* means an average thickness of the film which can be calculated from simple geometry of an experimental setup. Almost the same experimental setup for deposition is presented in the literature dealing with the production of Al–Pd–Mn quasicrystalline film reported by Saito et al. [14]. After deposition, the films were furnace-cooled below 100 °C within 90 min. The deposit films obtained were examined by using a 200 kV transmission electron microscope (JEOL JEM2010) with a resolution limit of 0.25 nm. The TEM instrument is equipped with a quantitative energy dispersive X-ray microanalysis (EDX) system, by which we performed chemical analysis for the TEM samples. The structural analysis of the films was supplemented by scanning electron microscopy (SEM; JEOL JSM-5900LV) as well as X-ray diffraction analysis (RIGAKU RINT2000/PC IN-PLANE) with Cu Kα radiation under an accelerating voltage of 40 kV and a beam current of 40 mA. Besides, the surface topography of the film samples was investigated in air by an atomic force microscope (SEIKO INSTRUMENTS: SPI3800N/SPA300HV), using a commercial Au-coated 100 μm triangular $Si_3N_4$ cantilever.

In any method of vacuum vapor deposition, the composition of deposited film is usually quite different from that of the mother alloy due to different vapor pressures of constituent elements. Almost all the thermodynamically stable QCs known to date require a strict condition in stoichiometry to form and accordingly the composition control during deposition is crucial to the success of the film preparation. Hence, we first searched for a possible range of alloy composition for the growth of d-phase in the resulting film. For this purpose, we prepared many pre-alloyed ingots of Al–Ni–Co having various compositions to use them as a deposition material. On the basis of data on these preliminary experiments, the composition of $Al_{72}Ni_{15}Co_{13}$ was finally selected as the deposition material. It was later confirmed by EDX analysis that the mother alloy with an

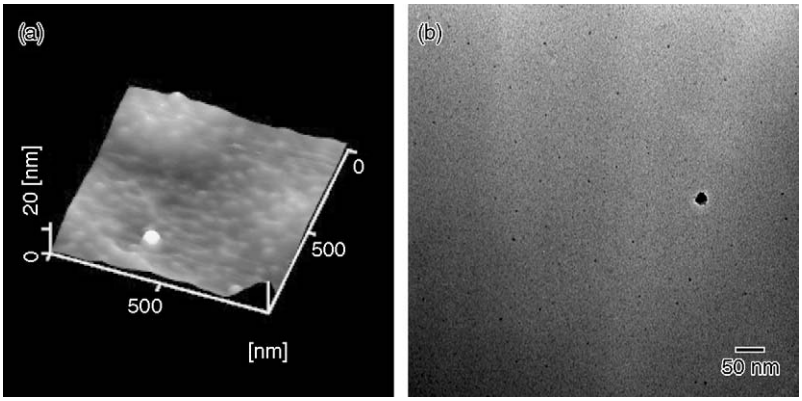


Fig. 1. (a) AFM image and (b) TEM bright-field image obtained from a bare substrate of a-C thin-foil.