We have grown nickel heteroepitaxially on muscovite and synthetic mica in vacuo for use as substrates for scanning probe microscopy (SPM) and graphene growth. We have determined annealing conditions that could generate atomically flat surfaces (with rms surface roughness of less than 1 nm). Owing to accelerated degradation at temperatures above 600 °C, muscovite mica was unsuitable as a substrate at high growth temperatures. Thermally stable synthetic fluorophlogopite mica [K(Mg3(AlSi3O10)F2)], on the other hand, was found to be stable at 800 °C and successfully employed for the formation of atomically flat films. © 2016 The Japan Society of Applied Physics

Since ultrahigh-vacuum scanning probe microscopy (UHV-SPM) is more surface-sensitive than other surface analysis techniques, the preparation of well-defined atomically flat and clean substrate surfaces is critical. It is well known that, during the development of the scanning tunneling microscopy (STM) technique, it was necessary to subject Si(111) sample substrates to degassing and flashing under UHV conditions in order to generate the now familiar Si(111)-7 × 7 surface.1,2) Furthermore, when investigating the nature of surface catalysts, in order to observe the structure and electronic states of a metal oxide surface, the preparation of a well-defined clean surface of a catalytic material such as TiO2 or SrTiO3 was also found to be important.3,4) Ideally, atomically clean single crystal surfaces of noble metals are often prepared using conventional methods such as a cycle comprising argon ion bombardment and annealing in a vacuum.5) Alternatively, Au(111) substrates are routinely used as the growth substrate of a self-assembled monolayer, which is not a bulk metal single crystal itself, and is often prepared by the evaporation of a gold thin film onto a mica substrate.6,7) In fact, such gold mica substrates are now commercially available.8,9) Clean single crystal surfaces of noble metals are often prepared using conventional methods such as a cycle comprising argon ion bombardment and annealing in a vacuum.10,11) In the area of surface science, graphene is referred to as “monolayer graphite”, since in the early 1990s researchers reported on the atomic level structure of CVD-generated graphene on high-temperature melting-point metal substrates such as Pt(111) and Ni(111).12-14) In general, a single crystal substrate should be subjected to precise cutting and polishing procedures which can be more costly than the deposited film substrate itself. Among the single crystals usually employed, Cu(111) is relatively inexpensive and tends to be more easily cleaned than high-melting-point metals. However, the temperature conditions required for graphene growth by hydrocarbon exposure on Cu(111) are close to the melting point of copper. In addition to the general difficulties associated with experimental conditions that require high-temperature control, the surface roughening of copper that can be observed with an optical microscope can occur.15) Since nickel has a higher melting point than copper, it is considered to be less prone to surface roughening at temperatures utilized for graphene growth. The utilization of a chemically active nickel surface allows for a lower graphene growth temperature than that required on copper. In fact, one report has described graphene growth on clean Ni(111) at 600 °C.16) Moreover, Odahara et al. reported that “Ni(111) is an exceptionally excellent substrate for commensurate graphene growth because of the small lattice mismatch by 1.2% and strong interfacial interaction and a single-domain sheet grew, and neither domain boundaries nor wrinkles were detected even by scanning tunneling microscopy at room temperature”.14,17,18) Although graphene may be grown on atomically flat metal substrates, wrinkles in the graphene create obstacles in terms of high-resolution SPM observation. Accordingly, we surmised that Ni(111) would be an excellent metal substrate for graphene growth since Ni(111) surfaces do not generate domain boundaries or wrinkles of graphene, nor do they lose their flatness during graphene growth.14,17,18) However, in order to prepare a clean surface of bulk single crystal Ni(111), the costs involved in removing impurities contained in the single crystal are far greater than those involved in the use of bulk single crystal Cu(111). Gerhard et al. reported that “A nickel single crystal always includes a considerable amount of contaminations and an atomically clean bulk single crystal Ni(111) could not be obtained by standard cleaning procedures”.19) To reduce the amount of impurities, one effective approach is to reduce the thickness of the single crystal to form a foil. Conversely, as in the case of gold mica, techniques for creating a metal thin film of a few hundred nm thickness on a flat mica substrate may be considered.20) One report that appeared in the 1970s detailed the deposition of nickel film on a muscovite mica substrate, without considering the surface flatness and its suitability for SPM.20) The report was about an investigation of the substrate temperature from room temperature to 650 °C. The report also indicated that a mica substrate for nickel film growth would be damaged at 600 °C or higher.21,22) Other reports have detailed nickel film growth on MgO substrates.23,24) MgO has a melting point of 2852 °C and is mainly used in the refractory industry. A lattice mismatch of 16% between Ni(111) and MgO(111) causes twin formation in large grains with macroscopic boundaries. Using a buffer layer technique, flat single-crystal nickel films can be heteroepitaxially grown on MgO(111) substrates. Since the preparation of an atomically flat and clean surface of a mica substrate can be achieved by
simple cleavage, with respect to applicability, we believe that inexpensive mica is very suitable for the heteroepitaxial growth of substrates for Ni(111). We consider that there are few reports detailing the use of Ni(111) on mica since the annealing temperature necessary for atomically flat film growth is higher than the decomposition temperature of mica. Recently, a synthetic mica of fluorophlogopite [KMg$_3$-(AlSi$_3$O$_{10}$)F$_2$] has been used as a substrate of heteroepitaxial growth of substrates for Ni(111). van der Waals) epitaxy given its atomically smooth surface, chemically inertness, and thermally stability even at a temperature of 1000 °C. In the present paper, the successful growth of atomically flat Ni(111) films on a synthetic mica substrate is described.

A nickel film was respectively deposited on a freshly cleaved fluorophlogopite mica substrate by evaporation from a homemade nickel wire (diameter 0.5 mm, Nilaco) basket under a base pressure of at least $1 \times 10^{-7}$ Torr. The thickness of the film was greater than 200 nm. When the film thickness was less than 200 nm, hexagonal voids were formed after annealing. All air AFM and ultrahigh-vacuum STM images were obtained using a Pico-Plus AFM (Molecular Imaging) system and an MFP-3D (Asylum Research) device in the AC mode (known as the tapping mode), and an Omicron LT-STM system, respectively. STM images were recorded under tunneling conditions with a sample bias ($V_s$) of $-2$ V and a tunneling current ($I_t$) of ca. 10 pA. Prior to STM imaging, Ni(111) films were cleaned in situ by standard cleaning procedures consisting of a few cycles of annealing and Ar$^+$ ion bombardment. The software programs used to perform the image processing were TIFS (Takeuchi’s Image Filing Software, http://www2.big.or.jp/osamu/TIFS/) and WSxM (http://www.nanotech.es/). The surface roughness (rms) of the obtained topographic images (the center 2.5 µm) was analyzed using WSxM. The X-ray diffraction data was measured at atmospheric conditions with a sample bias ($V_s$) of 2.5 V and $I_t$ of 5 pA, X = 2500 nm, Z = 5 nm, and $R = 0.64$ nm (rms) of nickel film ex situ deposited on a fluorophlogopite mica substrate annealed at 800 °C. Before STM observation, the sample surface was cleaned using a few cycles of annealing and ion sputtering. The STM image 

Figure 1(a) and 1(b) show AFM images of a synthetic mica substrate annealed at 700 and 800 °C, respectively, after nickel deposition. Note that nickel was first deposited on room-temperature synthetic mica substrates. After nickel deposition was completed, samples were annealed so that the temperature of the film can be optically monitored from outside of the chamber through a view port to allow for the precise control of temperature during annealing. The AFM image shown in Fig. 1(a) confirms that no notable evidence of thermal degradation of the synthetic mica substrate occurred owing to annealing at 700 °C. The surface roughness obtained from this AFM data of the nickel thin film is 4.2 nm (rms).

Since the surface roughness of gold on mica can be made smaller than 1 nm by relatively higher temperature annealing, further optimization of the annealing temperature was attempted by raising the annealing temperature to 800 °C. As a result, Fig. 1(b) shows the AFM image of a nickel thin film surface, indicating a typical surface morphology being that of a face-centered cubic (fcc) metal, i.e., facets with linear step edges along the $\{011\}$ directions (facets of hexagonal symmetry). The surface roughness obtained from this AFM image is 0.50 nm (rms), which is smaller than 1 nm (rms). In terms of the surface roughness and the fcc(111)-like morphology of the facets of hexagonal symmetry, we believe that the quality of this nickel film is comparable to that of commercially available gold mica.

The characterization of crystallinity was performed using XRD, as shown in Fig. 2. We performed $\theta/2\theta$ scan around the 111 peak of nickel [Fig. 2(a)], $\varphi$ scans of the $\{220\}$ peaks [Fig. 2(b)] and $\varphi$ scans of the $\{111\}$ peaks at $\chi = 70.5^\circ$ [Fig. 2(c)]. Both 700 °C (dotted line) and 800 °C (bold line) annealed nickel films turned out to be (111)-oriented films. The main difference between the two films was their crystallinity. Apparently, the quality of the film annealed at 800 °C was high. This result agrees well with the AFM data discussed above. Note that six (111) peaks separated by 60° [Fig. 2(c)] suggest the film is twin single-crystal.

Unlike gold, the clean surface of nickel is highly chemically active, and contamination is unavoidable when transferring samples from the deposition chamber to the STM chamber. Therefore, several cycles of Ar$^+$ sputtering and annealing were conducted in the preparation chamber connected to the UHV-STM chamber. This cleaning process removes radical contaminants due to exposure to the air, but may change the surface morphology. Figure 1(c) shows a typical large-area UHV-STM image (2.5 square microns), showing fcc(111)-like symmetry and atomic steps. The surface roughness obtained from this images is 0.64 nm (rms). It seems that the standard cleaning procedure comprising a few cycles of ion sputtering and annealing did not markedly change the surface roughness of the sample surface.

To measure the height of single atom steps, a narrower area of 630 nm width was imaged, as shown in Fig. 1(d). The cross section of the position indicated by a white dotted line in Fig. 1(d) is shown in Fig. 1(e). This cross section clearly shows an individual step height of 0.2 nm. Since the lattice constant of crystal nickel is 0.3524 nm, the smallest height difference (single atomic step) of fcc(111) is 0.203 nm. Thus, we can conclude that the observed atomically flat surface is Ni(111).
Note that the UHV-STM system used in this study did not comprise a thermal drift-free or variable temperature design. Two hours was usually required from the last sample annealed to stabilize STM imaging. It is known that a chemically active clean surface of nickel will be contaminated with background residual gases such as hydrogen and carbon monoxide molecules within an hour. Although there appear to be no obvious contaminants on the terraces or steps in the STM images, the Ni(111) surface in these STM images is probably covered with residual gases and thus may not be clean. Such contamination will occur regardless of whether a bulk single-crystal disk or deposited thin film is employed.

To the best of our knowledge, there are no reports detailing atomically flat (rms surface roughness <1 nm) Ni(111) film growth on mica substrates. We consider that the use of a thermally stable synthetic mica substrate allowed for a sufficient rise in annealing temperature to facilitate the migration of nickel atoms and the subsequent generation of an atomically flat thin film.

In conclusion, synthetic mica was employed as a substrate for thin film growth and an atomically flat Ni(111) thin film was heteroepitaxially formed. In addition to the small rms surface roughness achieved (<1 nm), the surface morphology appears to be comparable to that of commercially available gold mica. Film growth was not complicated and consisted of nickel deposition and substrate annealing. The authors expect that as long as synthetic mica and standard film growth techniques are available, our results can be reproduced easily. Although Ni(111) is one of the best metal substrates for high-quality graphene growth, we believe that the difficulty in preparing atomically flat Ni(111) substrates is stalling the progress of SPM research using graphene/Ni(111) substrates. We hope that this paper encourages the investigation and application of graphene, in addition to basic surface science research using SPM.

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Fig. 2. XRD patterns of two different types of Ni films on fluorophlogopite mica, annealed at 700 °C (dotted line) and 800 °C (bold line). (a) θ/2θ scan in the range of 44.0 to 45.0° (111 peak of nickel). (b) φ scans of the [220] peaks. (c) φ scans of the [111] peaks at χ = 70.5°.