Nuclear Instruments and Methods in Physics Research B 362 (2015) 133–137

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

In-situ GISAXS study on the oxidation behavior of liquid Ga on Ni(Cu)/Si substrates ☆

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ARTICLE INFO

Article history:
Received 22 March 2015
Received in revised form 31 August 2015
Accepted 22 September 2015
Available online 30 September 2015

Keywords:
GISAXS
Liquid gallium
Oxidation

ABSTRACT

Liquid Ga could be used as a flexible heat-transfer medium or contact medium in the synchrotron-radiation-based instruments. The chemical stability of liquid Ga on other metal surface determines the serviceability of liquid Ga. In this paper, the oxidation evolutions of liquid Ga on Ni and Cu substrates have been investigated by in-situ grazing incidence small angle X-ray scattering (GISAXS) as a function of substrate temperature. The liquid Ga on Ni and Cu substrates shows different oxidation behaviors. A successive and slower oxidation from oxide clusters to oxide layer takes place with temperature increasing from 25 to 190 °C on the surface of the Ga/Ni/Si specimen, but a quick oxidation occurs on the entire surface of the Ga/Cu/Si specimen at the initial 25 °C. The subsequent heating increases the surface roughness of both liquid Ga, but increases simultaneously the surface curvature of the Ga/Cu/Si specimen. The understanding of the substrate-dependent oxidation behavior of liquid Ga is beneficial to its application as a heat-transfer medium.

1. Introduction

Liquid gallium (Ga) has been widely investigated due to its unique physical, chemical and mechanical properties. For example, the influence [1,2] of Ga coverage and substrate temperature on the gallium structure on the Si(1 1 1)-(7 × 7) surface was monitored by low-energy electron diffraction (LEED) and synchrotron radiation photoelectron spectroscopy (SR-PES). A superconducting phase [3] of Ga film on thin Ni underlayer (0.1–5.0 nm) was evidenced at liquid-helium temperature because the thin seeding layer of Ni drove the subsequently grown Ga film into a pseudomorphic FCC structure. The optical properties of liquid Ga nanoparticles [4] embedded in a dielectric matrix were also investigated by using the spectroscopic ellipsometry. Recently, the oxidation behavior of metal Ga has attracted increasing attention due to the importance of corrosion in metallurgy and semiconductor technical applications of Ga sesquioxide [5,6]. The growth [7] of ultrathin Ga and Ga_2O_3 films on Ni(1 0 0) was investigated by using Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM). A thin amorphous Ga oxide was found to form on the top of a metallic Ga interlayer at 300 K. Further, a well-ordered thin film of γ'-Ga_2O_3 was formed via the coalescence and ordering of the Ga_2O_3 islands at 700 K. A logarithmic growth law [8] for the oxidation of liquid Ga and $Ga_{0.93}Hg_{0.07}$ in air was also reported by means of in-situ X-ray specular reflectivity. A pronounced layering [9] in the liquid density profile of liquid gallium metal in contact with a (1 1 1) diamond surface was observed by an X-ray scattering study. Recently, the adhesion of liquid Ga [10] on the surfaces of Ti, Nb, and Mo foils was studied. The results indicated that the Nb foil showed the minimum adhesion of liquid Ga to the surface, while the maximum amount of liquid Ga was observed to adhere to the Ti foil.

It is well known that the intense photon beams from the insertion devices of a synchrotron radiation photon source will have very high total powers on the optical elements. These high heat loads will require special cooling methods for the optical elements to preserve the quality of the photon beam. In these cases, liquid Ga is usually used as a heat transfer medium [11] in synchrotron radiation instruments. Even for an indirect cooling system of the high heat-load optical elements with water or liquid nitrogen,

☆ Supported by the National Natural Science Foundation of China with Grant Nos. U1232203, U1432104, 11405199, 11305198, U1332107 and the Program for Young Teachers Scientific Research in Qiqihar University (Grant No. 2012k-Z02).

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http://dx.doi.org/10.1016/j.nimb.2015.09.064
0168-583X/© 2015 Published by Elsevier B.V.

liquid Ga or Ga–In alloy is always used as the contact medium between the optical element and the cooling body due to their flexibility and very low vapor pressure. Therefore, the chemical stability of liquid Ga on other metal surface is crucial for the application of liquid Ga. Grazing incidence small angle X-ray scattering (GISAXS) [12–15] is a well-suited analytical technique because of its high sensitivity to the nanoscale electron density fluctuation. Areal-time GISAXS study [16] of Ga adsorption and desorption on *c*-plane sapphire as a function of substrate temperature and Ga flux has been reported. In this work, GISAXS technique has been employed to study the natural oxidation process and the surface morphology evolution of liquid Ga on Ni and Cu films sputtered on a Si(1 0 0) substrates.

2. Experiments

Ni or Cu film was deposited on a Si(1 0 0) substrate at room temperature (RT) by a FJL5600 magnetron sputtering system at an Ar flow rate of 17 sccm. The RF powers were 101 W and 98 W for Ni and Cu targets, respectively. Then liquid Ga was brushed on the Ni or Cu surface by means of a scalpel. GISAXS measurements for these samples were carried out at the beamline 1W2A of Beijing Synchrotron Radiation Facility (BSRF) with an incident X-ray wavelength (λ) of 0.154 nm. The storage ring was operated at 2.5 GeV with electron current of about 200 mA. A two-dimensional (2D) charge coupled device (CCD) detector with 2048 × 2048 pixels (pixel size ≈79 μm) was used to record the GISAXS patterns. This CCD detector was set to be perpendicular to the direct beam. The sample-to-detector distance was fixed at 5000 mm. First, the pixel position of the direct beam on the detector was recorded. Then, the top surface of sample was adjusted to parallel with the incident X-ray beam and was put into the X-ray path by controlling the support stage. Finally, the grazing incidence angle α_i with respect to the sample surface was set to and fixed at 0.3° for the Ga/Ni(Cu)/Si samples. The scattering angle with respect to the sample surface is defined as α_f, while the scattering angle in sample plane is defined as $2\theta_f$. The natural oxidation processes of the Ga/Ni/Si and Ga/Cu/Si specimens in air were monitored by in-situ GISAXS technique. As a heat-transfer medium or a heat-contact medium in synchrotron radiation instruments, the liquid Ga is generally used below 300 °C. Therefore, the specimens were heated from room temperature (RT, 25 °C) to approximately 295 °C at a heating rate of 10 °C/min in the oxidation process. Afterwards, the Ga/Ni/Si specimen was also kept at 295 °C for 9 min. Some GISAXS patterns at different heating temperatures were recorded. One dimensional GISAXS curves along the vertical direction of the GISAXS patterns (at $q_y = 0$) or along the horizontal direction of the GISAXS patterns (at $q_z \approx 0.36\ \text{nm}^{-1}$, or $\Delta q_z \approx 0.15\ \text{nm}^{-1}$) were extracted from these 2D-GISAXS patterns with the software Fit 2D [17] for further structural analysis. Here, the scattering vectors $q_y = (2\pi/\lambda)\cdot\sin(2\theta_f)\cdot\cos(\alpha_f)$, $q_z = (2\pi/\lambda)\cdot[\sin(\alpha_i) + \sin(\alpha_f)]$, and we define that $\Delta q_z = q_z - (2\pi/\lambda)\cdot\sin(\alpha_i) = (2\pi/\lambda)\cdot\sin(\alpha_f)$. A schematic map of the GISAXS measurements is shown in Fig. 1. Where P_d is the direct-beam position on the 2D detector, which is just the starting point of the q_z scattering vector. The direct-beam position P_d can be easily determined before the GISAXS measurements. P_0 is the position of sample-surface with a tile angle of 0.3° on the detector, which is the starting point of the Δq_z scattering vector. P_s is the specular reflection position. After the sample was well collimated to a grazing incidence angle of 0.3°, the specular reflection position P_s on the 2D detector can be accurately reproduced. P represents the position of an arbitrary scattering beam on the detector. Based on these special pixel positions, the collected 2D GISAXS patterns can be well calibrated.

3. Results and discussion

Two representative GISAXS patterns of liquid Ga on Ni/Si and Cu/Si substrates are shown in Fig. 2. In which Fig. 2(a) shows the GISAXS pattern of Ga/Ni/Si specimen at 150 °C and Fig. 2(b) shows the one of Ga/Cu/Si specimen at 150 °C. Although both GISAXS patterns are similar in a certain extent, their difference is clear from Fig. 2. As it will be shown in the following, this difference implies the different oxidation processes of liquid Ga on the different substrates during the heat treatments. In order to characterize the structure and ordering in the vertical or in plane direction of the liquid Ga thin films, the line-cut along the q_y-direction at $q_z \approx 0.36\ \text{nm}^{-1}$ or $\Delta q_z \approx 0.15\ \text{nm}^{-1}$ can be used to analyze the in-plane information such as the center-to-center distance of scatterers or their morphology, whereas the line-cut along the q_z-direction at $q_y = 0\ \text{nm}^{-1}$ can be used to analyze the structural information in the thickness direction of the films such as the scattering particle height or the possible lamellar structures. In this study, the line-cuts along the q_z and q_y directions are used to analyze and compare the oxidation behaviors of liquid Ga on the Ni/Si and Cu/Si substrates.

The line-cuts at $q_y = 0\ \text{nm}^{-1}$ of the Ga/Ni/Si specimen with different heat-treatment temperatures are compared in Fig. 3. It can be seen that a broadened scattering peak with peak position around $q_z \approx 0.42\ \text{nm}^{-1}$ or $\Delta q_z \approx 0.21\ \text{nm}^{-1}$ appears on the room-temperature line-cut. This peak position is just consistent with the position of specular reflection, so it can be attributed to the specular reflection. The broadening of the specular reflection could be mainly attributed to the bent surface (meniscus) and surface roughness of the liquid Ga film. However, the intensity of the specular reflection increases gradually from 25 to 190 °C, then decreases till disappearance from 190 to 295 °C. Whereas, the peak position (Δq_z) of specular reflection shifts in a faster rate from 0.21

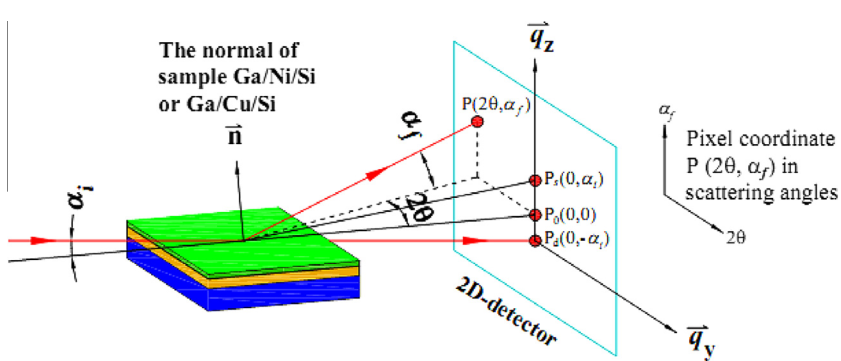

Fig. 1. A schematic map of the GISAXS measurements. The angular coordinates of several special scattering beams, as well as the q_y and q_z scattering vectors are given, which can be used to calibrate the GISAXS patterns.