Research of Transfer Technique of High-Quality Aluminum Thin-Film for Bio-Sensing

Kow-Ming Chang*, Yi-Ming Chen*, Kuang-Jen Lai*,1, Yu-Xin Zhang*, Chiung-Hui Lai**, Yi-Lung Lai**, Hui-Lung Lai**, Fu-Ching Lee**, and Chih-Hai Fan**

*Department of Electronics Engineering, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu, Taiwan 30010, R.O.C.
**Department of Electronics Engineering, Chung Hua University, Hsinchu 300, Taiwan, R.O.C.

ABSTRACT

The most common way in plasmonic bio-sensing is based on the angular modulation of surface plasmon resonance (SPR) combined with fluorescence spectroscopy. When the bio-molecules or nanoparticles attach on the metal film and change the resonant condition, we can detect the existence of specific bio-molecules by analyzing the change of optical properties. In the article, we introduce the transfer technique of ultra-smooth single-crystalline aluminum thin-film and may be applied as a sensor chip for the non-invasive plasmonic bio-molecular sensing. We report on the transfer result of high quality and ultra-smooth aluminum thin-film transferred onto an optical cover glass with root-mean-square roughness of 0.474nm. The transfer technique is based on the designed multi-epitaxial structures of Al, GaAs, AlGaAs, and GaAs substrate. Also, we use the properties of selective etching of citric acid and HF solutions for GaAs and AlGaAs.

Keywords: transfer, aluminum thin-film, plasmonic, bio-sensing

1 INTRODUCTION

Resonant plasmonic metal nanostructure can break the diffraction limit, concentrate the light into subwavelength dimensions and provide a strong near field enhancement [1,2]. Its unique optical properties has aroused many interests and has been applied to achieve surface-enhanced Raman spectroscopy [3], enhanced biochemical sensing [4,5], subwavelength optical waveguiding [6], index sensor [7], and optical trapping [8]. Among all the applied plasmonic materials, aluminum has attracted much more attention recently since its higher plasma frequency of about 15 eV as a potential competitive in ultraviolet (UV) applications compared with gold and silver of about 8 eV [9]. Gold and silver have been studied for their properties and chemical synthesis [10] as common plasmonic materials. The applications of gold and silver are mainly for visible to infrared spectral region since a strong interband transition exists at wavelength around less than 550 nm and 400 nm respectively [11]. On the other hand, the interband transition of aluminum occurs at about 800 nm, making it a suitable material for the UV-regime applications, including deep-UV surface-enhanced resonance Raman scattering [12], enhanced UV photocatalysis [13], aluminum-improved absorption in organic photovoltaic devices [14], and UV plasmonic nanolasers [15]. Also, the crystallinity affects the optical performance of nanostructures a lot, which has been demonstrated in the single-crystalline gold case [16]. Single-crystalline aluminum thin-film has been noted for its ultra-smooth surface and the lack of lattice boundaries, resulting in high-definition of nanostructures and high performance of optical responses [15,17]. However, there has not been a well-established method to obtain single-crystalline aluminum by chemical synthesis. The common way to grow a single-crystalline aluminum film through molecular beam epitaxy (MBE) on a GaAs substrate will drastically affect the effective optical spectrum since the optical responses from GaAs itself [17]. Therefore, single-crystalline aluminum thin-films applied in UV-regime is still a fancy topic. In this article, we are going to present the transfer of single-crystalline aluminum film grown in situ by molecular beam epitaxy from a GaAs substrate onto another substrate along with its analysis.

2 MATERIALS AND METHODS

Our single-crystalline aluminum thin-film is prepared following the previously reported works [17,18] with additional designed etching-stop layers. We use a Varian Gen II solid-source MBE system to grow our samples. After growing the 200 nm buffer GaAs on the semi-insulating (100) crystalline surface of GaAs substrate, a 500 nm Al0.9GaAs is grown on the buffer GaAs in the ultrahigh vacuum chamber (3×10-10 Torr). Next, we grow a 5 nm or 10 nm GaAs on the Al0.9GaAs layer. Then we grow the 40 nm aluminum thin-film at a rate of 0.05 nm/s, resulting in a crystalline surface of (110) aluminum. Use the plasma-enhanced chemical vapor deposition (PECVD) to deposit SiO2 for about 1.5 μm on aluminum at 300˚C which works as a new supporting layer. The schematic structure is shown in Fig. 1(a). The structures from top to bottom are 1.5 μm SiO2 / 40 nm Al / 5 nm or 10 nm GaAs / 500 nm Al0.9GaAs / 330 μm GaAs substrate with 200 nm buffer

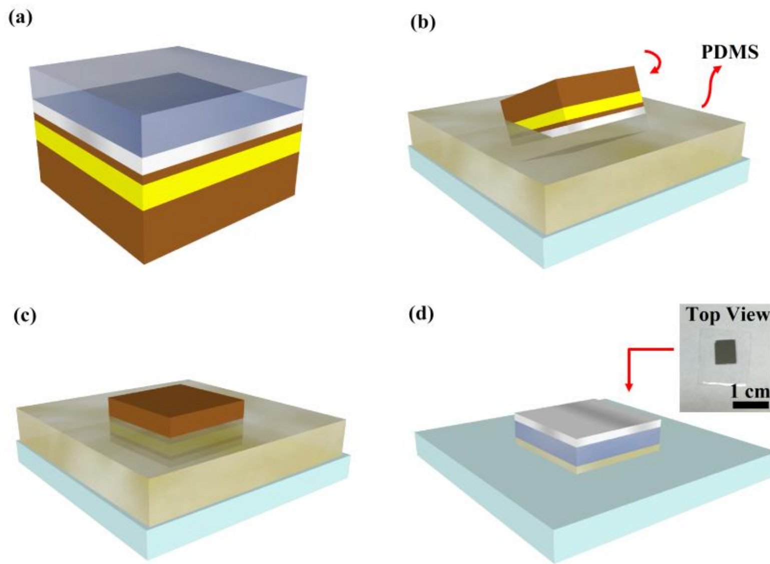

Fig 1: The schematic epitaxial structures and transfer processes. (a) The epitaxial structure with 1.5 μm SiO_2 evaporated by PECVD. (b) The schematic illustration of attaching the sample upside-down with the PDMS film. (c) The schematic illustration of the sample side-protection by PDMS. (d) The final result of the transferred sample.

layer. We have tried several thickness of the SiO_2, resulting in a limit abou 1 μm. If we didn't evaporate a supporting layer, the thin-film might wrinkle and split when we etch off the Al0.9GaAs layer. We can also deposit indium-tin-oxide (ITO) for conduction purpose instead of SiO_2 if needed. Prepare a polydimethylsiloxane (PDMS) mixture from SYLGARD® 184 SILICONE ELASTOMER KIT with a mixing ratio of part A : B = 10 : 1 and stir it evenly. Stand the PDMS alone for about 1 hour or just pumping it within a vacuum box for 30 min in order to let the air bubbles diminish. Then spin-coating the PDMS on the optical cover glass and attach the sample up-side-down with the PDMS, as shown in Fig. 1(b). It is worth noting that the optical cover glass can be replaced by an arbitrary substrate since we use the PDMS film as a bonding layer. Spin-coat the PDMS film with minimum 1000 rpm speed for 10s and maximum 6000 rpm for 30s. We evenly coat a 5 μm thickness of PDMS on the optical cover glass [19]. When we attach the sample with PDMS, it will work as a guard protecting the aluminum thin-film from side-etching, as shown in Fig. 1(c). Pumping it within a vacuum box for 30 min in order to let the air bubbles between the sample and the substrate diminish. Cure the PDMS by 80˚C for 30 min by hot-plate or oven. It is noted that any air bubble should be diminished before curing the PDMS or it might burst out through the thin-film when we etch off the Al0.9GaAs layer.

Use a grinder to grind the GaAs substrate down to less than 100 μm. Etch the residual GaAs wafer with citric acid solution : H_2O_2 = 5 : 1 by volume. The citric acid solution is prepared as anhydrous citric acid : deionized water = 1 : 1 by weight and should be prepared one day before etching so that the anhydrous citric acid would be fully dissolved. It will etch stop at the Al0.9GaAs layer at a speed of 314 nm/min.20 Then etch the Al0.9GaAs layer by H_2O : HF (49%) = 10 : 1 by volume and it will etch stop at the GaAs layer. The selective etching of Al0.9GaAs / GaAs in a HF system has been reported in detail [20,21]. Use another fresh citric acid solution : H_2O_2 = 5 : 1 by volume to etch off the thin GaAs layer at a speed of 314 nm/min. The step to etch off the GaAs layer must be quick in a few seconds to prevent from the further etching of aluminum. Finally, slowly press and pull the surrounding PDMS film and it will easily detach after immersing in HF solutions. Fig. 1(d) is the final transferred result shown with an inlet top view of a real sample. The structures are 40 nm Al / 1.5 μm SiO_2 / 5 μm PDMS / optical cover glass from top to bottom of 8 mm × 6 mm area.

3 RESULTS AND DISCUSSION

The RMS roughness of the transferred thin-film is 0.427 nm over 5 μm × 5 μm area, which is ultra-smooth as an untransferred epitaxial single-crystalline aluminum thin-film. As a comparison, we prepare a 200 nm electron-gun evaporated poly-crystalline thin-film. It is of 2.484 nm RMS roughness over 5 μm × 5 μm area, as shown in Fig. 2(b). The random voids and grains can cause the structural imperfections and optical signal scatterings [15,17]. Also, Reiss et. al. [22] has calculated the transmission probability of an electron through a single grain boundary of a poly-

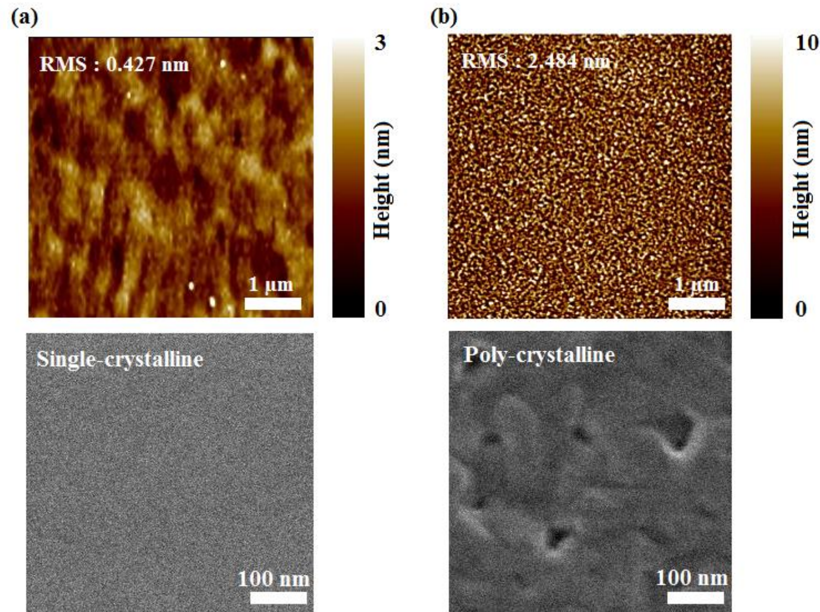

Fig 2: (a) Atomic force microscope (AFM) result of the transferred single-crystalline aluminum (top) and representative SEM image with ultra-smooth surface (bottom). (b) AFM result of the poly-crystalline aluminum (top) and representative SEM image (bottom).

crystalline metal film, resulting in the probability of 0.7 ± 0.1. It means that for about 30% of the electrons will be scattered when passing through a grain boundary elastically and inelastically. The scattering process will influence the electron-photon interaction and the performance of the plasmonic devices.

In Fig. 3(a), we compare the 2θ scanning X-ray diffracometer result of our transferred single-crystalline aluminum thin-film with a background signals which was measured without any sample on the XRD metal stage. The diffraction peak Al(220) occurred at 2θ = 65.35° is clearly detected without any GaAs diffraction peak [18]. Also, Fig. 3(b) shows the result of the optical reflectivity of the transferred sample and a 40 nm poly-crystalline aluminum film evaporated by conventional electron-gun system as a comparison. It shows that the transferred sample has higher reflectivity in the visible and UV regime as the untransferred case [17,18].

The energy dispersive X-ray spectroscope (EDS) results are shown in Fig. 4 with three different samples under process. Fig. 4(a) is the result of sample A with 10 nm GaAs etching stop layer. Fig. 4(b) is the result of sample B with 5 nm GaAs etching stop layer. Both of the two samples were etched and stopped at the GaAs layer through the transfer process. Fig. 4(c) is the result of sample C without 5 nm GaAs which has been etched off. By Comparing Fig. 4(a), Fig. 4(b), and Fig. 4(c), we confirm that the GaAs layer was etched off via rapid GaAs etching in a few seconds since Ga and As elemental signals are undetectable.

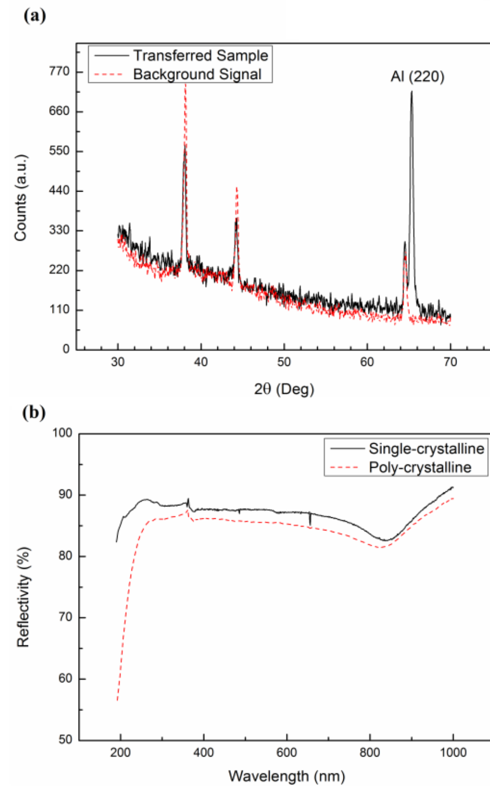

Fig 3: (a) The XRD result of the transferred sample (black-solid line) and the background signals (red-dashed line) which comes from the XRD metal stage. (b) The optical reflectivity of transferred single-crystalline aluminum (black-solid line) and poly-crystalline aluminum (red-dashed line) as a comparison

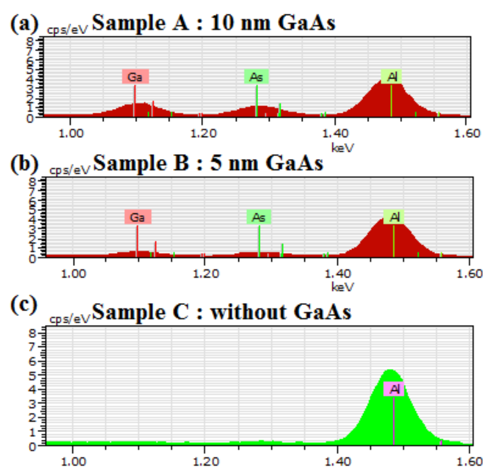

Fig 4: The EDS results of three samples with different GaAs thickness. (a) 10 nm GaAs. (b) 5 nm GaAs. Both (a) and (b) were etched and stopped at the GaAs layer. (c) The sample without 5 nm GaAs which has been etched off.

4 CONCLUSIONS

We present a process to transfer the single-crystalline aluminum thin-film from a MBE-grown GaAs substrate onto an optical cover glass. It is ultra-smooth, with a 0.427 nm RMS over 5 μm × 5 μm area and a higher optical reflectivity in the visible and ultraviolet regime compared with the poly-crystalline aluminum thin-film. The transfer process overcomes the influence of GaAs substrate and provides a method to obtain ultra-smooth single-crystalline aluminum thin-film on a new substrate, which can be applied in plasmonic and metal-based electronic devices.

REFERENCES

[1] W. L. Barnes, A. Dereux, and T. W. Ebbesen, Nature 424, 824 (2003)
[2] S. Kawata, Jpn. J. Appl. Phys. 52, 010001 (2013)
[3] P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. P. Van Duyne, Annu. Rev. Anal. Chem. 1, 601 (2008)
[4] J. Dostálek, and W. Knoll, Biointerphases 3, FD12 (2008)
[5] C. J. Huang, J. Ye, S. Wang, T. Stakenborg, and L. Lagae, Appl. Phys. Lett. 100, 173114 (2012)
[6] B. Steinberger, A. Hohenau, H. Ditlbacher, A. L. Stepanov, A. Drezet, F. R. Aussenegg, A. Leitner, and J. R. Krenn, Appl. Phys. Lett. 88, 94104 (2006)
[7] C. Y. Tsai, S. P. Lu, J. W. Lin, and P. T. Lee, Appl. Phys. Lett. 98, 153108 (2011)
[8] K. Y. Chen, A. T. Lee, C. C. Hung, J. S. Huang, and Y. T. Yang, Nano Lett. 13, 4118 (2013)
[9] D. Gérard, and S. K. Gray, J. Phys. D: Appl. Phys. 48, 184001 (2015)
[10] Y. Sun, and Y. Xia, Science 298, 2176 (2002)
[11] P. Biagioni, J. S. Huang, and B. Hecht, Rep. Prog. Phys. 75, 024402 (2012)
[12] S. K. Jha, Z. Ahmed, M. Agio, Y. Ekinci, and J. F. Löffler, J. Am. Chem. Soc. 134, 1966 (2012)
[13] M. Honda, Y. Kumamoto, A. Taguchi, Y. Saito, and S. Kawata, Appl. Phys. Lett. 104, 061108 (2014)
[14] V. Kochergin, L. Neely, C. Y. Jao, and H. D. Robinson, Appl. Phys. Lett. 98, 133305 (2011)
[15] B. T. Chou, Y. H. Chou, Y. M. Wu, Y. C. Chung, W. J. Hsueh, S. W. Lin, T. C. Lu, T. R. Lin, and S. D. Lin, arXiv,1505, 05650 (2015).
[16] J. S. Huang, V. Callegari, P. Geisler, C. Brüning, J. Kern, J. C. Prangsma, X. Wu, T. Feichtner, J. Ziegler, P. Weinmann, M. Kamp, A. Forchel, P. Biagioni, U. Sennhauser, and B. Hecht, Nat. Commun. 1, 150 (2010)
[17] H. W. Liu, F. C. Lin, S. W. Lin, J. Y. Wu, B. T. Chou, K. J. Lai, S. D. Lin, and J. S. Huang, ACS nano 9, 3875 (2015)
[18] S. W. Lin, J. Y. Wu, S. D. Lin, M. C. Lo, M. H. Lin, and C. T. Liang, Jpn. J. Appl. Phys. 52, 045801 (2013)
[19] J. H. Koschwanez, R. H. Carlson, and D. R. Meldrum, PLoS one, 4, e4572 (2009)
[20] J. H. Kim, D. H. Lim, and G. M. Yang, J. Vac. Sci. Technol. B. 16, 558 (1998)
[21] X. S. Wu, L. A. Coldren, and J. L. MERZ, Electron. Lett. 21, 558 (1985)
[22] G. Reiss, J. Vancea, and H. Hoffmann, Phys. Rev. Lett. 56, 2100 (1986)

[1]Corresponding author at: Department of Electronics Engineering,National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu, Taiwan 30010, R.O.C.
E-mail address: jessie80315@gmail.com (K. J. Lai).