Thin-Film light-trapping enhanced Quantum Dot photovoltaic cells (TFQD): an enabling technology for high power-to-weight ratio space solar arrays

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Optimized nanostructured ARC with Reflectivity less than 5% over the whole GaAs+QD spectrum (tentatively 400 nm-1300 nm)

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Abstract

This document provides an overview of the work done to optimize nanostructured ARC with reflectivity less than 5% over the whole GaAs+QD spectrum, more specifically the wavelength range of 400 nm-1300 nm. The fabrication process of is described in details including preparation of the nanostructures, their replications by nanoimprint lithography and pattern transfer by plasma etching process. Reflectance results of the nanostructured ARC samples are presented. This provides a background and knowledge to apply the nanostructures to the thin film solar cells as aimed in the project.

Change Records

Table I

Issue	Date	Change Record	Author
draft	14/1/2017	First release	T. Aho, T. Niemi, M. Guina
version 1.1	18/1/2017	Commented and corrected	F. Cappelluti, T.Aho, T. Niemi
version 1.2	6/10/2017	Fig.1 modified for public delivery	T. Aho

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List of Acronyms

AFM: Atomic force microscopy
ICP-RIE: Inductively coupled plasma - reactive ion etching
MBE: Molecular beam epitaxy
NIL: Nanoimprint lithography
PECVD: Plasma-enhanced chemical vapor deposition
RIE: Reactive ion etching
SEM: Scanning electron microscope
URA: Universal reflectance accessory
ORC: Optoelectronic Research Centre

1. INTRODUCTION

The light trapping structure of QD solar cells is divided to antireflection (AR) nanograting on top of the solar cell and micrograting reflector on the back surface. The simulations in T2.3 provided the initial structure and starting point to the development of the fabrication process. The generic light trapping and photon recycling structure for thin film QD solar cells is presented in Figure 1, where AR is fabricated to AlInP window layer and the back reflector is graded to polymer.

The aim for AR is to reach low, i.e. less than 5 %, reflectance in the wavelength region from 400 nm to 1300 nm. This is to done by nanoscale patterning of the window layer using nanoimprint lithography (NIL).

This document describes the fabrication process of the investigated ARC structures and the first results obtained. The process includes the preparation of the samples, NIL master and stamp preparation, NIL process and plasma etching of the structures. Optimization and characterization of the structures is still ongoing and the progress will be updated to this document.

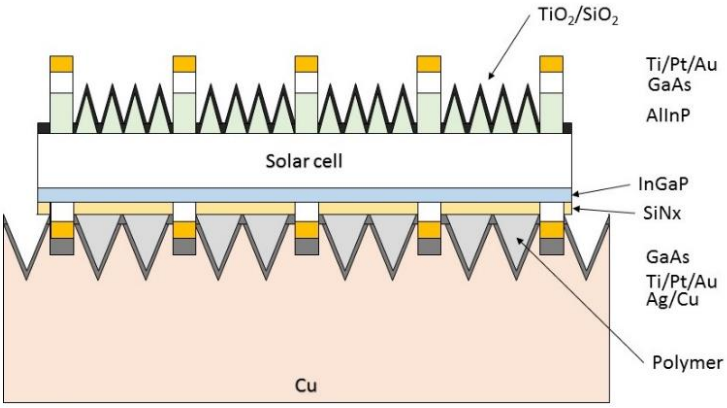

Figure 1. Generic structure of light trapping design.

2. ANTIREFLECTION COATING

The conventional ARC for solar cells consists of double-layer dielectric coating using e.g. ZnS/MgF_2 or SiO_2/TiO_2. The challenge with double-layer dielectric coating is to achieve low (<5 %) reflectance in the whole GaAs and QD wavelength range (400-1300 nm). The reflectance increases rapidly below 450 nm wavelength. Also in the wavelength of 600 nm the reflectance rises above 5 % [1]. To achieve lower reflectivity in broad wavelength range, nanostructure replicas of "moth-eye" patterns have been fabricated on different semiconductors including AlInP, which is commonly used as a window layer on GaAs-based solar cells [1]. To this end, we have devised a nanostructuring process employing NIL; the process flow is presented in Figure 2.

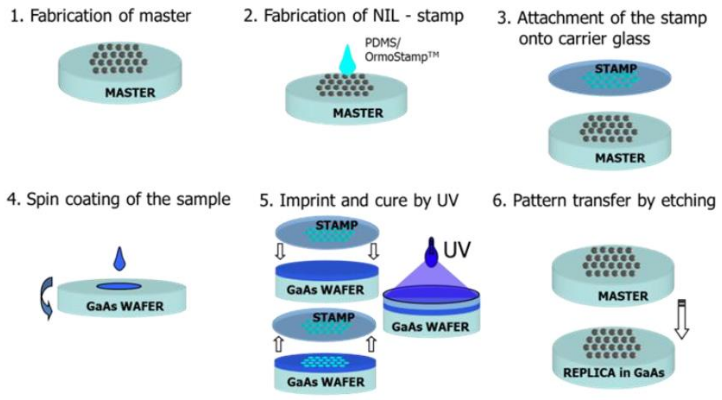

Figure 2. Process flow of the NIL.

As a background of the work, 300 nm period cone structure has been fabricated at ORC. However, to find the optimum structure and simplify the initial process, two different approaches are investigated. First is to fabricate cones with 180 nm period. The second approach is a pyramid structure with 180 nm period. The dependence of the structure period and the structure height to the reflectance was simulated using GD-Calc. The simulated structures were 3D AlInP pyramids on top of GaAs and the results are presented in Figure 3. According to the simulations, the pyramid height should be more than 400 nm and the period smaller than 400 nm, resulting in the reflectance less than 5 %.

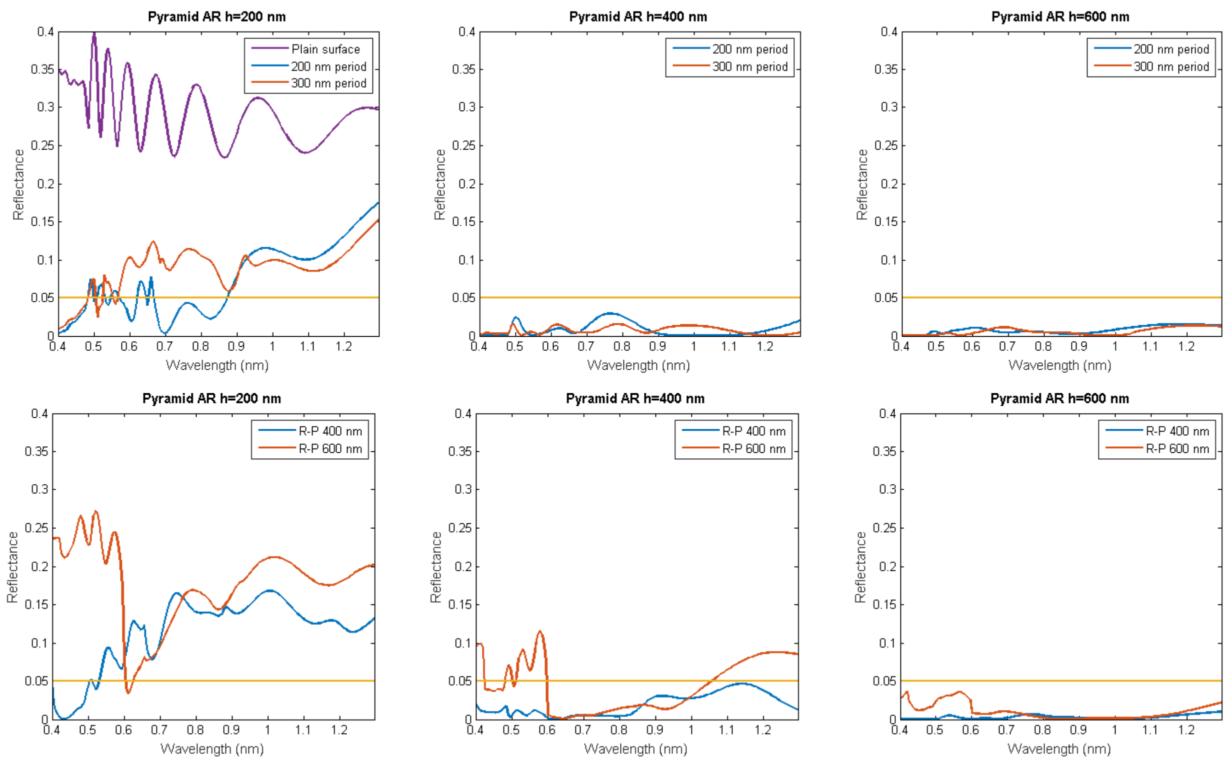

Figure 3. The simulated reflectance of the 3D pyramids on AlInP. The periods are 200 nm, 300 nm, 400 nm, and 600 nm. Pyramid heights are 200 nm, 400 nm and 600 nm.

2.1. Background: Fabrication of 300 nm period cones

The background of the fabrication process is cone structure with 300 nm period utilized on AlInP/GaAs samples grown by MBE. On top of AlInP layer, SiNx layer was grown by PECVD to act as an etch mask. [2]

The NIL master template was fabricated by lift-off process described in [3]. It consisted nanocones with a period of 300 nm. The master was used to fabricate the Ormostamp NIL negative replica stamp [4]. The cone pattern was imprinted to UV-NIL resist, which was used as etch mask to transfer the pattern to PECVD grown SiN_x. The transfer was performed using RIE etching with CHF_3/Ar based chemistry. The pattern was transferred from SiN_x to AlInP using ICP-RIE etching based on Cl_2/N_2/Ar chemistry. The SEM images of patterned AlInP are presented in Figure 4, which shows the formed cone shape structure. [2]

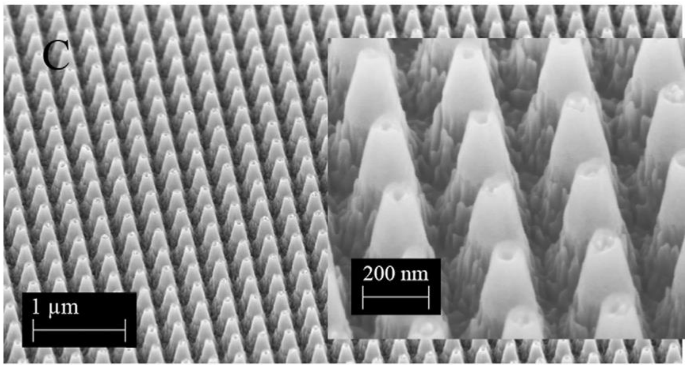

Figure 4. SEM images of 300 nm period cones. [2]

The measured reflectance of samples is presented in Figure 5. The measurements were performed using Accent RPM2000 mapping tool, which is taking only the reflected light at close to normal incidence. The red line is 300 nm period cone and the black line is the reference without any structuring. The reflectance of the 300 nm cone structure shows less than 5 % in the required wavelength of 400 nm - 1300 nm.

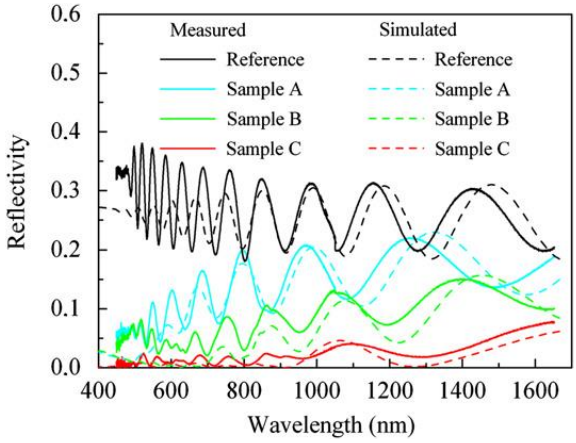

Figure 5. Simulated and measured reflectivity results of 300 nm period cones in AlInP is shown in sample C, red line. [2]

2.2. Fabrication of 180 nm period cones

Based on the simulation in Figure 3 (conducted with pyramids), 200 nm period structures were find out to have similar reflectivity behavior than 300 nm period structures. The NIL master with cylindrical holes, diameter of 90 nm at 180 nm period was used to fabricate the cone structure. A process, simpler than the 300 nm cones process, was devised and utilized to produce the structure.

The samples were AlInP layers grown by MBE on GaAs substrate. SiN_x layer were deposited using PECVD on top of the sample to act as etch mask. To perform the lift-off process, double layer UV resist, PMGI and mr-UVCur06, was spin coated into the sample surface, where the pattern was imprinted using NIL. The resist pattern was deepened with O_2 plasma etching using RIE and PMGI was removed from the opening with AZ 726 MIF developer (Merck Performance Materials GmbH). Thin Cr layer, 2 nm, was evaporated with electron beam evaporator. Cr from the top of the resist and the resist were removed with lift-off process and as a result Cr circle dots diameter of 90 nm were obtained. The pattern was transferred to SiN_x layer with CHF_3 and Ar chemistry plasma etching. Cr dots were acting as etch mask during RIE etch. Formed SiN_x cones are presented in Figure 6. The pattern was transferred to AlInP layer with ICP-RIE etching based on $Cl_2/N_2/Ar$ chemistry with flow rates of 10/15/2 sccm, respectively. The pressure was 3.0 mTorr and temperature 200 °C. The applied RIE chuck power was 50 W and ICP source power was 750 W. The etching was performed with separate etch steps to obtain the cone shape. The SEM image of the structured AlInP layer is presented in Figure 7. On top of the AlInP cones, 40 nm SiN_x layer with refractive index of 2.00 was evaporated using PECVD. SEM images of these cones are also presented in Figure 7.

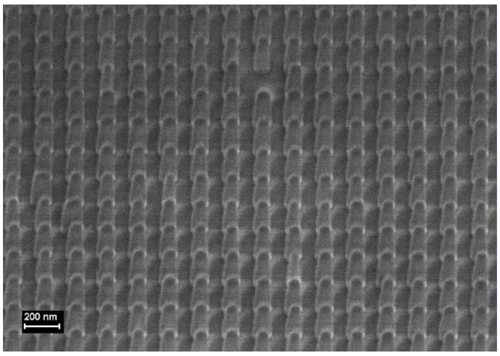

Figure 6. The structure transferred to SiN_x.

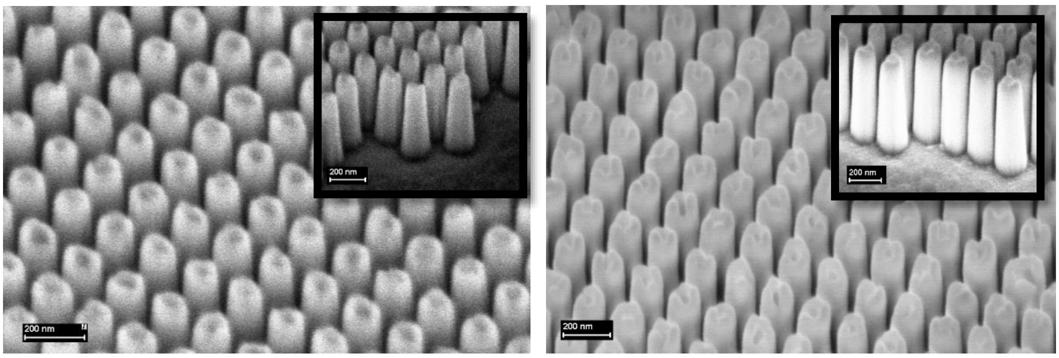

Figure 7. SEM images of 180 nm period cone structure in AlInP (left). Right image has 40 nm SiN_x layer of top of the AlInP cones.

The height of the 180 nm cones were approximately 500 nm, which was estimated from the SEM image. As presented in Figure 7, the 180 nm cones have rough surface on top of the cones. This undesired structure has an effect on the optical properties of the ARC. To achieve a perfect shape of the cone, more optimization of etching processes is needed.

The reflectance was measured form the samples before and after the SiN_x evaporation. Measurements were performed using PerkinElmer spectrophotometer with Universal Reflectance Accessory (URA), which is measuring the only the reflected light at close to normal incidence (8 degrees) and with an integrating sphere, which is measuring also scattered light. The result of the both measurements are presented in Figure 8.

The URA results show that the reflectance remains less than 5% from wavelength of 320 nm to ~950 nm for the sample without SiN_x layer and to ~1000 nm for the sample with SiN_x layer. The 40 nm SiN_x layer on top of the AlInP cones shifts the peak to the longer wavelengths. The highest peak of 9.4% reflectance is at wavelength of 1200 nm for the sample with SiN_x layer. As a reference GaAs solar cell with SiO_2/TiO_2 ARC is presented in the Figure 8.

In the measurements with integrating sphere, the light transmitted through the sample is reflected back from the white wall on the back of the sample. This is due to the samples have hardly any absorption below the band gap of GaAs. This can be seen in Figure 8, as the reflectance increases rapidly after 900 nm and the results are not representing the actual reflection from the surface. However, the reflectance below wavelengths of 900 nm remains low (< 5 %), which indicates light scattering is negligible.

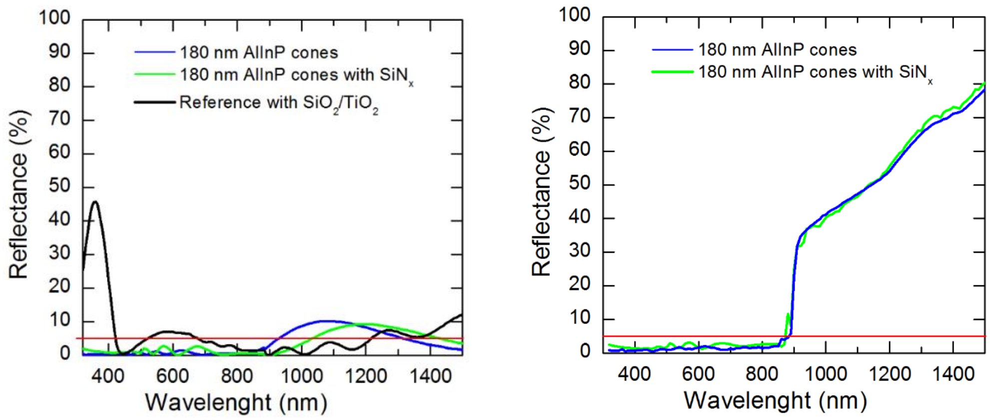

Figure 8. Reflectance results of 180 nm AlInP cone structure. The left figure is the URA results and the right is the integrating sphere results. The green line is the sample with 40 nm SiN_x evaporated on top of the AlInP cones and the red line represents the 5 % reflectance.

2.3. Fabrication of the 180 nm period pyramid structure

The simulations (Figure 3) indicated that less than 400 nm period pyramids have required reflectance, thus 180 nm period was selected. Pyramids should be higher than 350 nm, which were discovered from Figure 9, where the simulation of 180 nm period pyramid height on AlInP is compared to the reflectance.

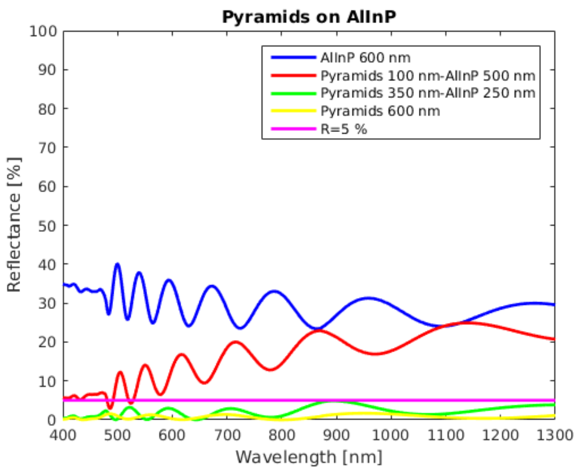

Figure 9. Simulation of 180 nm period pyramids on AlInP on top of GaAs substrate. The height of the pyramids is compared to the reflectance.

The initial NIL master had cylindrical holes with diameter of 90 nm at 180 nm period. The master was used to fabricate the Ormostamp NIL negative replica stamp [4]. The pattern in the stamp was transferred on Cr dots on silicon (100) wafer with the similar lift-off process as described in section 2.2. The Cr dots act as etch mask during the wet etching of silicon. The wet etching of silicon was performed with crystal plane selective etching, based on KOH chemistry. Finally, Cr was removed with commercial chromium etchant.

The SEM and AFM images of the master with 180 nm period pyramid structure are presented in Figure 10. From the AFM image the height of the pyramid was defined to be more than 100 nm, which is in the order of the theoretical height (120 nm) that will be achieved with KOH etching of silicon with an etch mask having a period of 180 nm. The height of the pyramid is increased using optimized transfer and etch process of the structure to the AlInP layer.

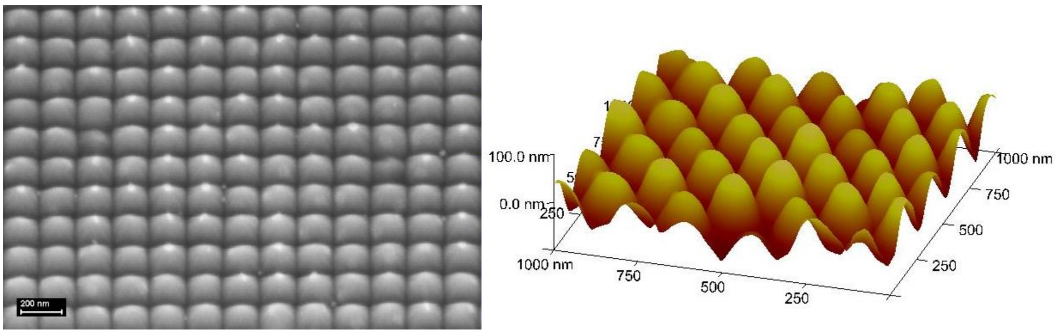

Figure 10. SEM (left) and AFM (right) images of the 180 nm pyramids on silicon NIL master.

To quantify the quality of the fabricated NIL master reflectance of the structure was simulated and measured using PerkinElmer spectrophotometer with an integrating sphere. The simulated and measured reflectance results of the silicon master with 180 nm pyramid structure are presented in Figure 11.

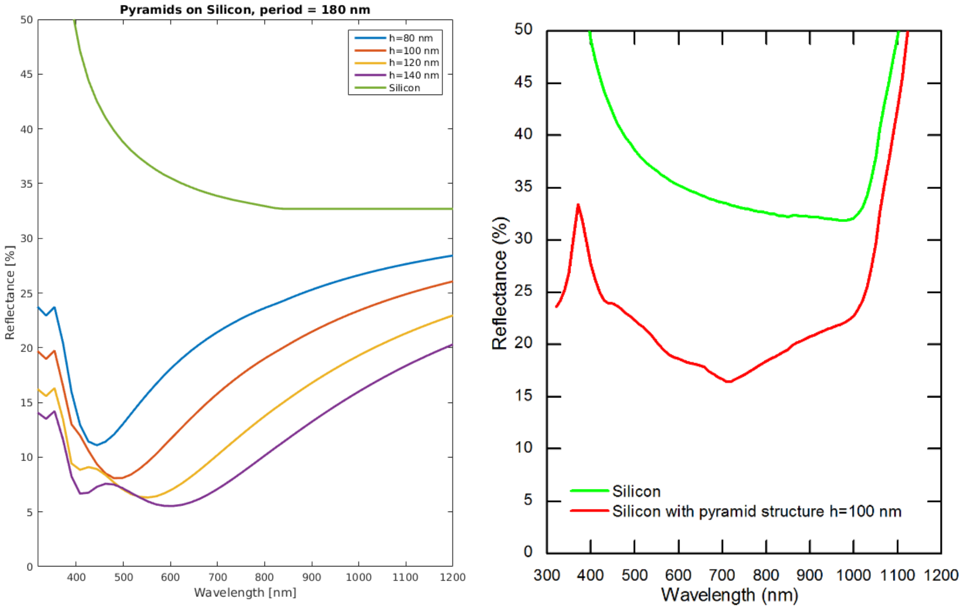

Figure 11. Simulated (left) and measured (right) reflectance results of 180 nm period silicon master with 180 nm period pyramid structure.

The reflectance results show that the trend of the simulations is present also in the measurements. The different between the simulated and measured results is due to the large beam size in the integrating sphere. The beam covers more than the uniform area of the pyramid pattern is in the master. Fabrication of large area pyramid master is challenging due to the KOH etching of Si. During the etching bubbles are formed which is causing difference in local etch rates and non-uniformity to the pattern. Some areas are etched faster and Cr mask is disengaging resulting in fast reduction of the pyramid height. Alternative crystal plane selective silicon etching solutions, that results in uniform etch rate, needs to be investigated.

Pyramid structured master was used to transfer the pattern to the AlInP layer with similar process as described in section 2.1. Optimization of the process and characterization of the structure is currently ongoing and will be added to this report.

3. CONCLUSIONS

In this report the fabrication of ARC with reflectivity less than 5 % over the GaAs and QD spectrum is described. ARC is fabricated with NIL on AlInP window layer. Two approaches are investigated. The first is based on cones with 180 nm period. The second approach is based on pyramids with 180 nm period.

The background of the investigation is the fabrication process of the samples with 300 nm cones. The NIL master with metal cones has been first fabricated and it has been used to imprint the pattern to the NIL resist. From the resist, the pattern has been first transferred to SiN_x and then to AlInP layer using plasma etching. The sample showed less than 5 % reflectance in the required spectral range.

The cone structure with 180 nm period has an advantage to have rather simple process and it is also applicable to large size areas (larger than 5x5 mm^2). The NIL master with cylinder holes was used to imprint the structure to the samples. Lift-off process were applied to achieve Cr circle dots to act as etch mask for cone etching. The cones were first etched to SiN_x and then transferred to AlInP layer using plasma etching. The top of the cone appeared rough, rather than desired smooth cone. More optimization of the plasma etching process is needed. The reflectance measurement showed promising behavior with reflectance of less than 5 % from wavelength of 320 nm to 1000 nm. The peak reflectance of 9.4 % was observed at the wavelength of 1200 nm.

According to the simulations, less than 400 nm period pyramid pattern showed optimal optical properties. The NIL silicon master with 180 nm period pyramids was fabricated using master with 90 nm diameter cylinders with 180 nm period. First Cr circle dots were produced using lift-off process. These Cr dots were acting as etch mask for crystal plane selective wet etching of silicon with KOH based chemistry. The pyramids were achieved, though uniform large areas are challenging to produce, due to the formation of bubbles during the wet etching. The pattern was imprinted to AlInP, but more process optimization is needed before the results are completed. The result of the pyramid shape pattern will be updated once the iteration is completed.

4. REFERENCES

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