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Chemical compatibility of fused filament fabrication-based 3-D printed components with solutions commonly used in semiconductor wet processing

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ABSTRACT

3-D printing shows great potential in laboratories for making customized labware and reaction vessels. In addition, affordable fused filament fabrication (FFF)-based 3-D printing has successfully produced high-quality and affordable scientific equipment, focusing on tools without strict chemical compatibility limitations. As the additives and colorants used in 3-D printing filaments are proprietary, their compatibility with common chemicals is unknown, which has prevented their widespread use in laboratory chemical processing. In this study, the compatibility of ten widely available FFF plastics with solvents, acids, bases and solutions used in the wet processing of semiconductor materials is explored. The results provide data on materials unavailable in the literature and the chemical properties of 3-D printable plastics that were, are in line with literature. Overall, many 3-D printable plastics are compatible with concentrated solutions. Polypropylene emerged as a promising 3-D printable material for semiconductor processing due to its tolerance of strongly oxidizing acids, such as nitric and sulfuric acids. In addition, 3-D printed custom tools were demonstrated for a range of wet processing applications. The results show that 3-D printed plastics are potential materials for bespoke chemically resistant labware at less than 10% of the cost of such purchased tools. However, further studies are required to ascertain if such materials are fully compatible with clean room processing.

1. Introduction

3-D printing has shown considerable promise in chemical labs in the fabrication of chemical reactionware [1–4], millifluidics [5,6], microfluidics [7–10], and continuous flow chemistry [11]. In addition, accessible fused filament fabrication (FFF)-based 3-D printing [12–14] (also called fused deposition modeling (FDM) under trademark and material extrusion as stated in ISO/ASTM 52900:2017-02), has been shown to be effective at fabricating high-quality, bespoke, low-cost scientific equipment [15–17]. For example, digital re-creation of devices have been demonstrated for chemical mixing [18–20], biotechnological and chemical labware [20–24], colorimeters and turbidimeters [25–27], liquid autosamplers [28], and fluid handling [29,30], as well as mass spectroscopy equipment [31]. In general, this approach reduces capital cost of scientific equipment by 90–99% compared to conventionally produced equipment [20,32], which has created substantial value for the scientific community [32]. This past work, however, has focused primarily on equipment without strict chemical compatibility standards or the use of known reagent-grade materials.

As the exact chemical formulation of low-cost commercial 3-D printing filaments (as well as additives such as plasticizers and colorants) is proprietary and thus chemical compatibility of printed parts is unknown, there has been no significant 3-D printing use in more challenging laboratory environments, such as those of clean rooms used for semiconductor processing. Due to the high cost of even basic equipment in clean rooms there is thus an opportunity to save funds while improving custom equipment with the use of 3-D printing. Furthermore, due to the high infrastructure and operation cost of the cleanroom, it is particularly important to improve the process throughput to fully utilize the facilities. In a multidiscipline research-orientated clean room and industrial R&D facilities, significant time is spent on overcoming equipment limitations, because the equipment is installed to serve a wide range of research interests instead of the

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optimum for every process. Thus, 3-D printed accessories based on individual process requirements have the potential to improve cleanroom throughput as well as reducing processing costs by, for example, reducing the consumption of chemicals needed for processing. In order to exploit these opportunities, this study provides laboratory and cleanroom workers a materials toolkit for making their own reliable, customized, and chemically resistant labware from affordable materials using accessible FFF-based 3-D printers, as alternatives for commonly used polypropylene and fluoropolymer tools.

2. Materials and methods

Specifically this study evaluates the chemical compatibility of 3-D printing polymers with wet chemical treatments commonly used in the clean room processing of semiconductor devices. We determine their chemical compatibility with common solvents and wet etchants using a down selection process. First, a range of commercial 3-D printing polymers is immersed in a range of common cleanroom chemicals for one week while monitoring mass and dimension changes after both surface and vacuum drying. These results are subsequently compared to chemical compatibility information available in the literature (chemical resistance charts from Curbell Plastics, Sirmax, Thermo Fisher Scientific and Plastics International) for the pure plastic that correlates to the main component of the filament. The 3-D printing materials considered are: polylactic acid (PLA), polyethylene terephthalate glycol (PETG), 2 different co-polyesters (Eastman Amphora AM3300-based nGen and Amphora 1800-based Inova-1800), polypropylene (PP), acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA), polyamide copolymer-Nylon 6/69 (taulman3D Alloy 910), polyethylene terephthalate (PET, taulman3D t-glase), and polycarbonate (PC). The properties of the studied materials are summarized in Table 1.

The simple chemicals tested in the first phase are deionized water (DI H_2O), isopropyl alcohol (IPA), acetone, ethanol, hydrochloric acid (HCl, 37%), ammonia (NH_3, 25%), hydrogen peroxide (H_2O_2, 30%), phosphoric acid (H_3PO_4, 85%), nitric acid (HNO_3, 69%), sulfuric acid (H_2SO_4, 95–97%), and acetic acid (100%). While many of the chemicals are generally used as dilute solutions, the 3-D printable plastics are immersed in concentrated solutions to study the upper limit of their chemical compatibility. If a plastic is compatible with a concentrated solution, it will most likely tolerate diluted solutions of the same chemicals for extended times. The studied chemicals are summarized in Table 2. Deionized water was obtained from the Micronova cleanroom water plant facilities (resistivity > 18 MΩ-cm). Other studied chemicals were obtained from commercial vendors (ethanol from Altia Plc / Technical Ethanol, Rajamäki, Finland, all others from Honeywell Specialty Chemicals Seelze GmbH, Seelze, Germany).

The experiments were divided into three phases: Phase 1 is the immersion of filaments in a single chemical, while in Phase 2 3-D printed rectangular pieces of the materials that showed acceptable compatibility were immersed in the same chemicals. Based on the results of Phases 1 and 2, sui Table 3-D printable materials were selected for case studies based on their chemical tolerance and ease to print (e.g. no delamination and printable on a standard FFF type 3-D printer with no alterations). Printed samples that pass the tests are analyzed with differential scanning calorimetry (DSC) to evaluate changes in the crystallinity, glass transition and melting temperatures of the polymers, which are closely linked to, amongst other factors, polymer chain structure, repeating unit type and length, molecular weight, branching, additives, etc. [33,34]. The materials that withstand the simple chemical environments are then tested in more demanding chemical processes and solutions commonly used in semiconductor device fabrication: photoresist strip, RCA 1 and RCA 2 cleaning, hydrogen fluoride (HF) dip, Aqua regia immersion, and Piranha immersion [35]. In addition, in Phase 3 open source parametric 3-D printable laboratory tools were immersed in the solutions. In the down selection process, a ± 5% change in mass or dimensions of the sample was used as the acceptance criterion, but in determining the practical compatibility of the polymers with specific solutions a stricter ± 1% criterion was considered.

Table 2
Studied single chemicals, their formulae, concentrations and use in wet processing.

Chemical	Formula	Concentration [%]	Use
Deionized water	H_2O	–	Common solvent
2-propanol (isopropanol, IPA)	$CH_3CHOHCH_3$	100	Organic solvent
Acetone	CH_3COCH_3	100	Organic solvent
Ethanol	$(CH_3)OCH_3$	95	Organic solvent
Hydrochloric acid	HCl	37	RCA 2, Aqua regia
Ammonia solution	NH_3,	25	RCA 1
Hydrogen peroxide	H_2O_2	30	RCA 1, RCA 2
Orthophosphoric acid	H_3PO_4	85	Al etching
Nitric acid	HNO_3	69	Si etch, Aqua regia
Sulfuric acid	H_2SO_4	95-97	Piranha
Acetic acid	CH_3COOH	100	Al etching
Hydrofluoric acid	HF	50	SiO_2 etch, cleaning

Samples for Phase 1 were prepared from FFF materials as received from the manufacturer. All samples were handled with nitrile gloves to protect the filaments from contaminants resulting from skin contact. 20–25 mm long strands of filament were cut from the spools using conventional scissors cleaned with IPA. All individual pieces of filament were weighed with a VWR (Radnor, PA, USA) precision scale and their diameters were measured using a digital caliper with an accuracy of ± 0.01 mm. After preparation, the samples were placed into

Table 1
3-D printing materials arranged by 3-D printing nozzle temperature.

Plastic	Product name	Supplier	Color	Cost [\$/kg][a]	Print *T* [^{O}C]
PLA	Polylite PLA	Polymaker	True Blue	25	205
PETG	PETG	Octofiber	Natural	53	225
Eastman Amphora 3300	nGen	Colorfabb	Lulzbot green	52	230
Eastman Amphora 3300	nGen	Colorfabb	Red	52	230
PP	PP	Ultimaker	Natural	98	235
ABS	ABS	IC3D	Green	40	245
Eastman Amphora 1800	Inova-1800	Chroma Strand	Blue	80	245
ASA	ASA Extrafill	Fillamentum	Traffic Black	42	250
Polyamide copolymer-Nylon 6/69	Alloy 910	taulman3D	Black	79	255
PET	t-glase	taulman3D	Green	66	255
PC	PC-Max	Polymaker	Black	61	255

[a] Price estimates are obtained from suppliers online stores specialized in 3-D printing.