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High mobility single-crystalline-like silicon thin films on inexpensive flexible metal foils by plasma enhanced chemical vapor deposition

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ABSTRACT

In this report, we demonstrate heteroepitaxial growth of single-crystalline-like Si thin films on inexpensive and lightweight flexible metal foil substrates using radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD). Single-crystalline-like Ge thin film on ion-beam textured templates on metal foils served as epitaxy enabling substrates for Si growth. The epitaxial Si films were oriented along (004) direction and strongly biaxially-textured with narrow in-plane and out-of-plane spreads. Surface morphology was granular with 300–400 nm diameter grains having very low-angle grain boundaries (average ~ 0.5°). Raman spectroscopy revealed near 100% crystallinity and high structural quality, comparable to bulk c-Si wafer. Controllable in-situ gas phase doping was carried out to achieve n- and p-type Si films with high electron and hole mobilities of 230 and 65 cm^2/V-s respectively and carrier concentrations suitable for electronic device application. Direct deposition of high mobility single-crystalline-like Si thin films on flexible and inexpensive metal foils can be a potential route towards roll-to-roll scalable manufacturing of high-performance flexible electronics applications.

1. Introduction

Mechanically flexible electronic and energy harvesting devices have gained a lot of attention in recent years. Flexible electronic devices, fabricated on bendable and light-weight substrates, have a broad range of novel market applications, including wearable electronics, printed sensors, memory, displays, electronic skin, and flexible solar cells.[1–4] Currently, single-crystalline silicon (c-Si) based devices and circuits dominate the microelectronics market. High carrier mobility, natural abundance and environmental benign nature of c-Si along with mature manufacturing technology have further made c-Si the material of choice for most integrated electronic applications. However, c-Si technology requires rigid, brittle and bulky single-crystal Si wafers to grow c-Si thin films used as active layers in devices, limiting scalable large-area processing and flexible electronics applications. If high-quality c-Si thin films with device-quality electrical properties can be developed on inexpensive flexible substrates, it will not only further reduce cost and weight of electronic devices by eliminating the Si wafers, but also open up opportunities for novel applications of flexible electronic devices beyond traditional technologies. The use of flexible substrates can potentially enable large-area and scalable roll-to-roll manufacturing of c-Si thin film printed electronics.

Efforts to achieve c-Si thin films on flexible platforms have been largely focused on epitaxial lift-off and transfer printing techniques, where epitaxially grown Si thin films are separated from wafer substrates and transferred on to desired flexible substrates for device fabrication.[5–9] Others have employed post-deposition techniques such as excimer laser annealing and metal-induced crystallization of disordered Si thin films grown on flexible substrates to obtain c-Si-like properties, mainly higher carrier mobilities.[10–12] However, technical effectiveness and commercial viability of these indirect processes are yet to be proven. Attempts have been made to develop ultra-thin Si device components which can be picked and placed on flexible platforms for flexible hybrid electronics (FHE) applications.[13] However, true conformity, flexibility and scalable processing have not been achieved. Therefore,

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direct growth of c-Si thin films on low-cost flexible substrates by standard deposition techniques is highly desirable for economic and scalable mass production of printed flexible electronics.

Growth of c-Si films by standard deposition techniques (typically by chemical vapor deposition) requires crystalline lattice-matched substrate, capable of withstanding high-temperature epitaxial growth processes. These conditions are well met by c-Si wafers which allow homoepitaxial growth of c-Si films. However, finding an alternate flexible substrate with appropriate crystal structure for epitaxial Si growth has remained a challenge so far. Direct deposition of Si on flexible non-crystalline substrates has yielded amorphous (a-Si) or polycrystalline Si (poly-Si) films with much lower carrier mobilities compared to c-Si, thereby rendering them unsuitable for high-performance devices. For instance, deposition of Si on polyimide and plastic substrates at temperatures below the low thermal degradation limit of the substrates (usually <300 °C) resulted in a-Si or poly-Si with carrier mobilities typically less than 1 cm^2/V-s.[14] Attempts made to deposit Si on glass substrates for display applications have also resulted in low-mobility (<20 cm^2/V-s) a-Si and p-Si films [15]. The low carrier mobility significantly limited the performance and efficiency of the displays and devices. a-Si was obtained when Si was directly deposited on metal foils as well [16]. Clearly, there is a substantial opportunity for performance improvement if high-mobility Si can be achieved by direct deposition on alternate platforms.

A promising alternative approach to grow epitaxial single-crystalline-like semiconductor thin films on non-crystalline flexible substrates employing standard deposition techniques is the template or “seed and epitaxy” technique using cube-textured foil substrates [17,18] In this process, starting with a flexible non-crystalline substrate, a biaxially-textured template is developed to meet the lattice and thermal-match requirements of the desired semiconductor epilayer, which is then grown using standard deposition methods. Additionally, the starting flexible substrates (most often metals) and intermediate buffer layers are chosen to sustain high temperature growth processes. Two primary “seed and epitaxy” approaches include the Ion-beam Assisted Deposition (IBAD) [18,19] and Rolling-Assisted Biaxially-Textured-Substrates (RABiTS) [17] techniques. In fact, the IBAD template technique is a well-established and industrially scaled up process employed to grow biaxially-textured high-temperature superconductors (HTS) on metal foils. [20,21] It has also been used to grow semiconductor films on textured templates with low-angle grain boundaries which are relatively less detrimental to the electrical properties of the films [18].

Biaxially-textured single-crystalline-like Ge and III-V GaAs thin films have already been developed on textured flexible substrates, exhibiting high carrier mobilities. [22–25] Efforts have also been made to develop biaxially-textured single-crystalline-like Si thin films on flexible substrates. Findikoglu et al. first demonstrated the growth of biaxially-textured Si thin films by e-beam evaporation on flexible, polycrystalline Hastelloy metal foils using ion-beam-textured IBAD MgO buffer layer and intermediate epitaxial γ-Al_2O_3 template layer as the epitaxy enabler. [26] The films were boron doped p-type and exhibited a hole mobility of 89 cm^2/V-s. No n-type doping was reported. J. R. Groves et al. demonstrated growth of biaxially-textured Si thin films by hot-wire chemical vapor deposition (HWCVD) on display glass using ion-beam-textured IBAD CaF_2 buffer layer. [27] HWCVD of single-crystal-like Si thin films with (004) orientation on Al_2O_3 coated biaxially textured RABiTS Ni-W metal foils have also been demonstrated. [28,29] It is to be noted that till now, HWCVD and e-beam evaporation have been the primary method of choice to grow biaxially-textured Si on flexible substrates. Up to now, one of the most popular and widely used CVD deposition methods in the semiconductor industry, radio-frequency plasma-enhanced chemical vapor deposition (RF-PECVD), has not been explored. Moreover, a comprehensive study of gas phase in-situ n and p-type doping of Si films on flexible substrates has not been demonstrated yet.

In this report, we demonstrate heteroepitaxial growth of undoped, n and p-type single-crystalline-like Si thin films on IBAD templates on flexible, polycrystalline metal foils using conventional RF-PECVD. Here, we employed remote inductively-coupled plasma (ICP) to generate ahigh-density plasma, thereby promoting epitaxial growth at lower temperatures while causing significantly less ion-bombardment damage to the film surface. [30,31] RF-PECVD was chosen since it is one of the most popular techniques to grow device-quality crystalline thin films at lower temperatures and is often with improved electrical properties compared to HWCVD or e-beam evaporation. [32,33] Single-crystalline-like Ge thin film on IBAD template on inexpensive metal foil, developed by roll-to-roll deposition processes, was used as substrates [23]. Si hetero-epitaxy was explored over a wide growth temperature regime (700–900 °C) and gas flow rates. Biaxially-textured Si films were obtained with sharp in-plane and out-of-plane texture, with a strong (004) orientation. Gas phase in-situ doping was carried out using phosphine (PH_3) and diborane (B_2H_6) gases. Controllable doping (from moderate to high doping) was achieved for both p- and n-type Si films. High electron mobility of 230 cm^2/V-s was obtained in n-type Si films. Hole mobility of 65 cm^2/V-s was obtained in p-type Si films. We have demonstrated Si thin film transistors (TFT) on metal foils in a recent publication however a comprehensive study of the materials properties and growth conditions have not been reported yet. [34] This paper provides a detailed study of the CVD growth conditions and microstructural properties of single-crystalline-like flexible Si thin films including the evolution of biaxial texture, in-plane and out-of-plane texture spreads, grain misorientation and optical-phonon vibrational properties.

2. Experimental details

Si thin films were deposited in a modified Plasmalab100 (Oxford instruments) chemical vapor deposition system using an inductively-coupled plasma reactor operated at 13.56 MHz radio frequency. A high-temperature heating stage capable of reaching up to 1100 °C was retrofitted to the deposition chamber. Though epitaxial Si growth has been reported at lower temperatures on c-Si wafers [32,35] achieving hetero-epitaxy on biaxially-textured flexible templates was quite challenging and required higher growth temperatures (>600 °C). Therefore, a combination of high growth temperature and dense inductively-coupled remote-plasma was employed to achieve crystal growth on flexible templates. Meter-long tapes of single-crystalline-like Ge thin film on metal foil were cut into short pieces (1.2 cm wide, 6 cm length) and loaded on an inconel sample holder, specially designed to hold flexible samples. Furthermore, corrosion resistant and high-temperature compatible Hastelloy C-276 metal foil (50 µm thick) did not produce any detectable contamination to the reactor and enabled deposition of Si at elevated temperatures. The chamber base pressure was 2.5×10^{-7} Torr. The samples were transferred in and out of the reactor using a load-lock assembly, which helped to keep the chamber clean and in high vacuum during the sample transfer process, enabling high purity and reproducible film quality. Si films were deposited at an optimized plasma power of 300 W and deposition pressure of 75 mTorr, at growth temperatures ranging from 700 to 900 °C. The process gases consisted of high purity silane SiH_4 (6N) and hydrogen purified by a palladium cell purifier to high level purity. Hydrogen dilution was used (SiH_4-to-H_2 ratio was 1:4) during Si growth in order to promote crystallinity