Concentric ring pattern formation in heated chromium-gold thin films on silicon

Jatinder S. Randhawa,[1] Adam Bernfeld,[1,a)] Michael Keung,[1] Alex A. Volinsky,[2] and David H. Gracias[1,b)]
[1]*Department of Chemical and Biomolecular Engineering, Johns Hopkins University, 3400 N. Charles Street, Baltimore, Maryland 21218, USA*
[2]*Department of Mechanical Engineering, University of South Florida, 4202 E. Fowler Ave. ENB118, Tampa, Florida 33620, USA*

(Received 21 April 2008; accepted 6 May 2008; published online 28 May 2008)

Patterns that formed spontaneously upon heating thermally evaporated thin films of gold (Au) and chromium (Cr) on silicon (Si) substrates to 500 °C were investigated. A variety of patterns were observed. The type of pattern formed correlated with the thickness ratio of Cr to Au. The most striking pattern consisted of concentric rings spaced approximately 10–30 μm apart. Each ring was composed of pits 2–5 μm in length, which extended 200–400 nm into the silicon substrate. While concentric patterns are widely seen in chemical reaction-diffusion systems, pattern formation in the heated Au/Cr/Si system has not been previously observed. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2937309]

The spontaneous formation of ordered patterns, out of equilibrium, is scientifically intriguing since this phenomenon is characteristic of living systems; these patterns have been widely observed in chemical reaction-diffusion systems.[1,2] Pattern formation has also been observed in some metallic thin film systems; these include patterns formed in gold (Au) films deposited on polymers due to mismatch in thermal expansion,[3] in flash-annealed tantalum films on silicon (Si),[4] and in laser-induced recrystallization of nanoscopic metal films.[5]

In this letter, we describe the spontaneous patterns observed when Si wafers coated with thermally evaporated Au and chromium (Cr) thin films were heated to 500 °C. Au and Cr thin films on Si are widely used in microelectronic, biosensor, and microelectromechanical systems. Cr improves adhesion of Au to the underlying Si substrate. Upon heating, Cr and Au can interdiffuse and react with Si. This intermixing and reaction impacts the performance and reliability of thin film circuits and devices fabricated with these materials.[6,7] Additionally, the Cr/Au/Si system represents a complex yet interesting test bed for studying reaction-diffusion based pattern formation. Reaction-diffusion systems are those wherein two or more chemical species react while simultaneously spreading by diffusion. We have systematically studied pattern formation with varying Cr/Au thickness ratios; however, we focus on an ordered concentric circular pattern that was found when heating Au/Cr/Si films with a Cr/Au thickness ratio (R) of approximately 1.3 (65 nm Cr, 50 nm Au).

In our studies, Au and Cr were thermally evaporated (10^{-5} Torr) at different thickness ratios on commercial 75 mm Si wafers at the rate of approximately 0.01 nm/s for 1 nm, 0.05 nm/s for the following 4 nm, and then at 0.1 nm/s for the remaining thickness. It should be noted that the native oxide (SiO_2) on Si was present in our studies and influenced the temperature at which pattern formation occurred, as described later. We studied pattern formation by uniformly heating the Au/Cr/Si substrates from room temperature to 500 °C over a period of 10 min. The temperature was then maintained at 500 °C for 1 h. The temperature at the surface of the wafer was measured using infrared thermometry and a calibrated thermocouple.

We observed a variety of patterns when heating Au/Cr/Si(100) films with different thickness ratios (Fig. 1 and see EPAPS[8]). In the absence of Cr (i.e. Au/Si), circular mounds [Fig. 1(a)] 1–2 μm high were observed, when heated above 370 °C. We believe that the circular features in the Au/Si system are a result of a eutectic reaction between Au and Si. A eutectic reaction results in the formation of a liquid phase from two solid phases upon heating. Au and Si undergo a eutectic reaction at 363 °C with a Si mole fraction of 0.186.[9] We observe, from Fig. 1(a), that the Au reacts with the Si only at specific nucleation sites. This inhomogeneous reaction can be attributed to the presence of the native SiO_2 barrier and the high atomic ratio of Au required for eutectic formation.

When Cr films as thin as 2.5 nm (R=0.05) were deposited between the Au and Si, the circular features disappeared and rectangular parallelepiped-shaped pits were observed [Fig. 1(b)]; moreover, these pits appeared only when the wafers were heated to a higher temperature of approximately 500 °C. The pits were observed at other Cr/Au ratios as well. We outline the primary reactive and diffusive processes that occur when wafers with Cr inserted between Au and Si are heated. Cr is known to diffuse through thin films of Au to the air-Au interface where it becomes oxidized.[10] In some of our films with high Cr/Au ratios, we observed a greenish color after heating, characteristic of Cr_2O_3;[11] Cr also reacts with Si to form chromium silicides.[12] The pits on the Si (100) wafers were outlined by crystallographic planes parallel and perpendicular to the wafer flat; on Si (111) substrates (at R=1.3) triangular pits were observed. The exact mechanism for the formation of crystallographically faceted pits is not entirely clear; however, evidence for both oxide and silicide reactions was obtained from Auger depth profiles on

a)Present address: DuPont Experimental Station, Wilmington, DE 19880-0302.
b)Author to whom correspondence should be addressed. Tel.: +1 410-5165284. FAX: +1 410-5165510. Electronic mail: dgracias@jhu.edu.

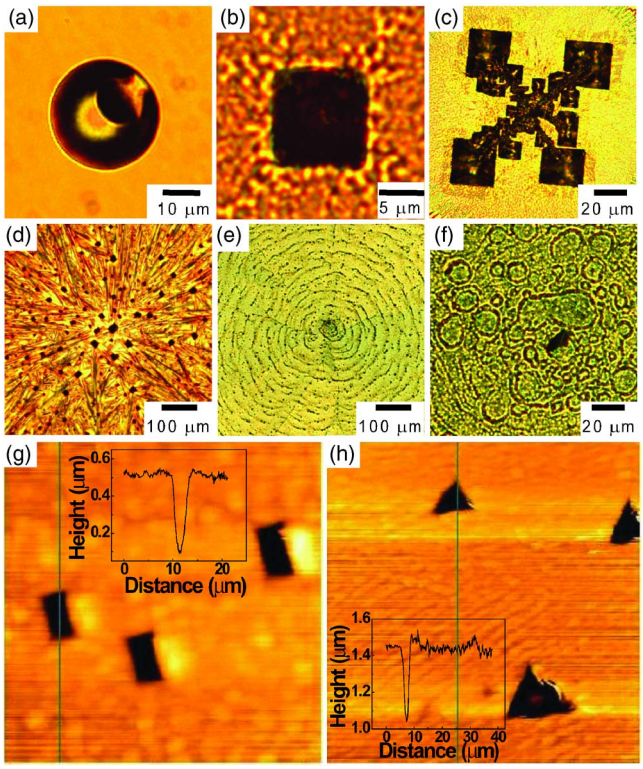

FIG. 1. (Color online) The patterns observed on heating Au/Cr/Si with varying Cr/Au ratio R. (a) At $R=0$ (0 nm Cr, 50 nm Au), circular mounds were observed at random locations on the Si(100) wafer. (b) At $R=0.05$ (2.5 nm Cr, 50 nm Au), rectangular parallelepiped-shaped pits were observed at random locations on the wafer. (c) At $R=0.2$ (10 nm Cr, 50 nm Au), polyomino structures were observed. (d) At $R=0.4$ (20 nm Cr, 50 nm Au), starburst patterns were observed. (e) At $R>0.9$, e.g., $R=1.3$ (65 nm Cr, 50 nm Au) concentric patterns were observed. (f) At $R=3.25$ (65 nm Cr, 20 nm Au), nonconcentric Turing-like patterns were observed. (g) AFM images of rectangular parallelepiped pits observed (at $R=1.3$) on the Si(100). (h) Triangular pits observed (at $R=1.3$) on the Si(111) substrate.

heated wafers (see EPAPS[8]). Regarding the higher temperature at which the features were observed (pits at 450–500 °C for Au/Cr/Si versus circular mounds at 370 °C for Au/Si), we note that the intermixing of Au and Si is prevented by the Cr layer, until it is depleted. Cr can be depleted by diffusing to the air interface where it gets oxidized or by reacting with the underlying Si. The reaction of Cr with the underlying Si is prevented by the SiO_2 until around 450 °C.[13] Hence, the native oxide is an important barrier in the intermixing of Cr and Si at lower temperatures. This barrier is thin however and can be bridged at temperatures above 450 °C, allowing intermixing of Cr, Si, and subsequently Au.

Systematically increasing the Cr/Au ratio dramatically altered the arrangement of the pits. Hence, while at $R=0.05$ isolated pits were observed, when the ratio was increased to 0.2, the pits were arranged in a polyomino structure [Fig. 1(c)]. These patterns are reminiscent of those observed in epitaxial growth of Au on Si.[14] At higher thickness ratios of 0.4, starburst patterns were observed [Fig. 1(d)]. However, at ratios above 0.9, concentric circular patterns appeared [Fig. 1(e)] and eventually formed circular but nonconcentric Turing-like patterns [Fig. 1(f)].[2]

Here, we focus on the concentric patterns observed when the Cr/Au thickness ratio was about 1.3. These patterns, consisting of rectangular and triangular pits, were observed on both Si(100) and Si(111) substrates [Figs. 1(g) and 1(h)].

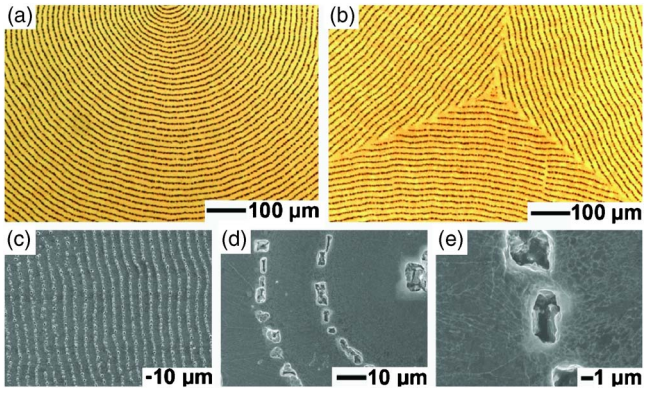

FIG. 2. (Color online) (a) Concentric ring pattern formed on heating an aged Au/Cr/Si(100) wafer with Cr/Au at $R=1.3$. The spacing between two consecutive rings was approximately 20 μm. (b) Optical image at the boundary of fronts from three different nucleation sites. [(c)–(e)] SEM images of the concentric ring pattern at increasing magnification.

When the Si substrate was replaced with glass or alumina, the patterns did not form, indicating that pure Si was needed for pattern formation. We also observed no pattern formation when Cr and Au were evaporated on Si wafers with a thick (500 nm) thermally grown oxide. Additionally without Au or Cr, no patterns were observed. Hence, Au, Cr, and Si are all needed for circular pattern formation.

While we were able to repeatedly reproduce the concentric patterns at ratios of 0.9 to 1.3, (patterns at $R=1.3$ were reproduced on films deposited in two different evaporators), their quality and definition varied. As stated earlier, we discovered these concentric patterns while heating Si(100) wafers with a Cr/Au thickness ratio of approximately 1.3, as estimated by Auger depth profiling. Initially, we found the patterns forming on wafers that had been evaporated over a year prior to the heating experiments. These patterns had extremely high quality as compared to freshly evaporated samples [compare Fig. 2 to Fig. 1(e)], indicating that ageing may also influence the pattern quality.

The concentric patterns were extensively characterized using a combination of optical, electron, and atomic force microscopy in addition to Auger electron spectroscopy. The individual pattern features were rectangular pits [but more irregular than those observed in Fig. 1(b)] with their long axis perpendicular to the propagation direction of the rings. Some of the features within each ring were interconnected. The ring pattern originated from multiple locations at different nucleation sites on the wafer and propagated outward in the radial direction at the rate of approximately 14 μm/s until the entire sample surface area was covered with the pattern (see EPAPS[8]). When two or three pattern fronts came together, a boundary was formed as seen in Fig. 2(b). In the boundary, there was a distinct region where no patterns were observed (i.e., the patterns from adjacent fronts did not merge into each other). A surface topographic analysis (Fig. 3) shows that the pattern features are pits that extend 200–400 nm deep into the Si substrate. Energy dispersive spectroscopy (EDS) maps of Si, Au, and Cr, along with the corresponding scanning electron microscopy (SEM) image of the micron sized pattern elements taken at 30 KeV were obtained (Fig. 3). It should be noted that at this electron beam energy, the electron beam penetration depth in Au, Cr, and Si is greater than the film stack thickness of 70 nm. EDS maps show that the features consisted of pits rich in both Au

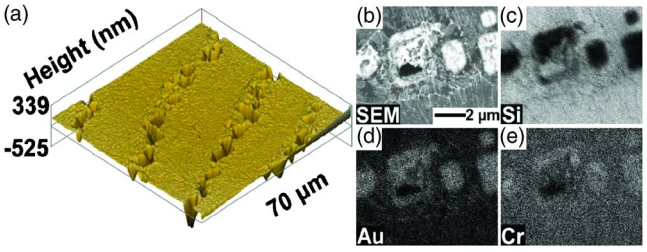

FIG. 3. (Color online) (a) Depth profile of the concentric pattern shown in Fig. 2. (b) SEM image of individual features in the pattern and [(c)–(e)] EDS maps of Si, Au, and Cr, respectively. Brighter regions in the map correspond to higher concentration of the respective element.

and Cr. Sometimes a small region was observed within the pit that was rich in Si. Auger depth profiling (see EPAPS[8]) was performed on the wafer before and after heating. Before heating, the wafer showed the Au/Cr/Si stack as expected with intermixed interfaces. However after heating, the top layers were covered with Cr and O (O from the oxidized chromium at the surface), while the Au and Cr had diffused into the Si substrate.

We believe that the patterns are formed due to a combination of reaction and diffusion. Upon heating, the Cr diffuses through the Au to the Au-air interface where it oxidizes, thus preventing its diffusion back toward the Si. This results in Au moving closer to the Si interface. However, Au has to be in excess and in contact with Si to form a eutectic. Although the Au–Si eutectic starts to form at 363 °C, this reaction is prevented by the dense Cr layer separating Au from Si. Above around 450 °C, the Cr breaks through the native oxide and reacts with the Si. Subsequently, chromium is involved in two reactions: chromium oxide formation at the air interface and chromium silicide formation at the Cr/Si interface. Initially, the Cr would react with Si at defect sites in the oxide layer. Once Cr begins to react with Si, Au can also react with Si at certain nucleation sites, since Cr would deplete at the Au/Cr interface due to its reaction with Si. Hence, at this interface there is a competition between Au and Cr to form their respective silicides and intermixing of Au, Cr, and Si.

In order to form a eutectic, the Au has to be in excess, and we believe that after nucleation, there is a driving force for more Au to move toward the nucleation site, resulting in a depletion of Au in surrounding regions. Hence, waves of high Au concentration surrounded by regions of low Au concentration are formed and propagate radially. One piece of evidence for this conclusion is that the pitch of the rings decreased with increasing Au thickness. Assuming that the Au–Si eutectic is achieved in the features, it would require Au:Si to be in a molar ratio of approximately 4:1. Hence, with a thicker Au film, less Au is needed from the surrounding areas to provide the excess Au required to initiate the eutectic reaction with Si. Our data reflected this conclusion such that at ratios from 0.9 to 1.3, 25 nm thick Au had a pitch of 50 μm, 50 nm thick Au had a pitch of 25 μm, and 75 nm thick Au had a pitch of 10 μm. One more piece of evidence is that when the patterns from different nucleation sites came in contact with each other, they never merged (because the pattern fronts were immediately surrounded by regions of low Au concentration).

In conclusion, we have observed a variety of patterns in Au/Cr/Si thin film stack, including a concentric ring pattern. The proposed mechanism is complicated by the fact that thermodynamic, diffusion, and kinetic constants for this system are unavailable and are moreover affected by the thickness, age, and deposition conditions. Hence, further quantitative measurements of thermodynamic and kinetic parameters combined with theoretical modeling are necessary to elucidate the exact types of patterns formed at different Au/Cr ratios, as well as the size, shape and number of pits formed within each pattern. We do believe though that the important reaction and diffusion processes occurring have been outlined. In addition, we believe that apart from being intriguing, these patterns may be important for the reliability of thin film devices and in templating patterns.

The authors acknowledge NSF-MEXT support for the US-Japan Young Scientists Symposium on Nanotechnology and Nanomanufacturing. A.V. acknowledges the support from NSF Project Nos. CMMI-0631526, CMMI-0600231, and CMMI-0600266 related to the reported results. D.H.G. acknowledges funding from NSF (Career-044816). We acknowledge the help of Justin Gorham, Dr. Howard Fairbrother, and the JHU Materials Science Center with Auger spectroscopy, and Mark Koontz and Timothy Leong for EDS mapping.

[1] I. R. Epstein and J. A. Poojman, *An Introduction to Nonlinear Chemical Dynamics: Oscillations, Waves, Patterns, and Chaos* (Oxford University Press, New York, 1998).
[2] M. C. Cross and P. C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1993).
[3] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, and G. M. Whitesides, Nature (London) **393**, 146 (1998).
[4] H. Y. Sheng, D. Fujita, Z. C. Dong, H. Okamoto, T. Ohgi, and H. Nejoh, J. Vac. Sci. Technol. B **17**, 2565 (1999).
[5] C. Favazza, J. Trice, R. Kalyanaraman, and R. Sureshkumar, Appl. Phys. Lett. **91**, 043105 (2007).
[6] N. R. Moody, D. Adams, A. A. Volinsky, M. Kriese, and W. W. Gerberich, *MRS Symposia Proceedings No. 586* (Materials Research Society, Pittsburgh, 2000), p. 195.
[7] N. R. Moody, D. P. Adams, D. Medlin, T. Headley, N. Yang, and A. A. Volinsky, Int. J. Fract. **119/120**, 407 (2003).
[8] See EPAPS Document No. E-APPLAB-92-004822 for Auger depth profile spectra of the Au/Cr/Si film stack before and after heating, a comprehensive list of images documenting patterns formed at different ratios of Cr/Au and for real time video clips of the pattern formation. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[9] T. B. Massalski and H. Okamoto, *Binary Alloy Phase Diagrams*, 2nd ed. (ASM International, Materials Park, OH, 1990).
[10] G. Majni, G. Ottaviani, and M. Prudenziati, Thin Solid Films **38**, 15 (1976).
[11] D. R. Lide, *CRC Handbook of Chemistry and Physics* (CRC, Boca Raton, FL, 2007).
[12] E. G. Colgan, B. Y. Tsaur, and J. W. Mayer, Appl. Phys. Lett. **37**, 938 (1980).
[13] K. H. Baether, G. Zies, R. Voigtmann, W. Moldenhauer, and H. Schreiber, Thin Solid Films **188**, 67 (1990).
[14] K. Sekar, G. Kuri, P. V. Satyam, B. Sundaravel, D. P. Mahapatra, and B. N. Dev, Solid State Commun. **96**, 871 (1995).