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Pulsed KrF laser annealing of $Mo/Si_{0.76}Ge_{0.24}$

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Abstract

Interfacial reactions of $Mo/Si_{0.76}Ge_{0.24}$ were studied by pulsed KrF laser annealing as a function of the energy density and pulse number. Vacuum annealing was also performed on some samples for comparison. For the samples annealed at a temperature of 500–700°C a continuous hexagonal $Mo(Si_{1-x}Ge_x)_2$ (h-$Mo(Si_{1-x}Ge_x)_2$) film was formed, while Ge segregation from the h-$Mo(Si_{1-x}Ge_x)_2$ film to the underlying $Si_{0.76}Ge_{0.24}$ occurred with the extent becoming more severe at higher annealing temperatures. Concurrently, amorphous structures appeared in the $Si_{0.76}Ge_{0.24}$ substrate. At 700°C h-$Mo(Si_{1-x}Ge_x)_2$ transformed to tetragonal $Mo(Si_{1-x}Ge_x)_2$ (t-$Mo(Si_{1-x}Ge_x)_2$). Multiple-pulse laser annealing could produce a continuous h-$Mo(Si_{1-x}Ge_x)_2$ film without forming amorphous structures in the $Si_{0.76}Ge_{0.24}$ substrate, however, it could not suppress Ge segregation. In the present study, no t-$Mo(Si_{1-x}Ge_x)_2$ was formed upon pulsed KrF laser annealing even at higher energy densities. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: $Mo(Si_{1-x}Ge_x)_2$; Pulsed KrF laser annealing; Ge segregation; Amorphous structures

1. Introduction

Recently, strained $Si_{1-x}Ge_x$ epitaxial layers on Si have been extensively studied for potential applications in optoelectronic and high-speed electronic devices [1]. For device applications the formation of metal/$Si_{1-x}Ge_x$ ohmic or rectifying contacts is required. Thus, the interfacial reactions of some metals such as Ni [2–4], Pt [5,6], Pd [6–9], Ti [10–15], Co [16–20], W [21,22], Cr [23], Cu [24,25] and Zr [26] on $Si_{1-x}Ge_x$ by conventional furnace annealing, rapid thermal annealing, and pulsed laser annealing have been studied, respectively. For conventional furnace annealing the formation of a ternary phase is generally accompanied with Ge segregation. Additionally, an agglomeration structure also appears at higher annealing temperatures. These phenomena could be attributed to the higher heat of formation for metal-Si than for metal-Ge [27]. Rapid thermal annealing [12,13] and pulsed laser annealing [3,4,9] can shorten the annealing time, resulting in a reduction of Ge segregation. Furthermore, pulsed laser annealing can produce a smooth and continuous germanosilicide film without inducing strain relaxation in the unreacted $Si_{1-x}Ge_x$ film [9].

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Refractory metals and refractory metal silicides have a higher temperature stability that makes them attractive candidates for contact metallizations in ultra-large-scale integration circuits. The interfacial reactions of W on $Si_{1-x}Ge_x$ have been studied by conventional annealing and rapid thermal annealing, respectively [21,22], where Ge segregation may increase the barrier height. As we know, however, the $Mo/Si_{1-x}Ge_x$ system has not been studied yet. In this work, the interfacial reactions of Mo on $Si_{0.76}Ge_{0.24}$ were studied by pulsed KrF laser annealing as a function of energy density and pulse number. Simultaneously, vacuum annealing of $Mo/Si_{0.76}Ge_{0.24}$ was also conducted for comparison.

2. Experimental

Epitaxial $Si_{0.76}Ge_{0.24}$ films about 1500 Å thick were grown on n-type Si(1 0 0) at 550°C by ultra-high-vacuum chemical-vapor deposition (CVD). Prior to Mo deposition, the substrates were cleaned by the RCA method and then immediately loaded into the chamber. Mo about 200 Å thick was deposited onto the $Si_{0.76}Ge_{0.24}$ films at 200°C by electron gun evaporation at a rate of 1 Å/s. The base pressure was around $1–2 \times 10^{-6}$ Torr. Vacuum annealing was carried out at a temperature of 450–700°C in a vacuum of $1–2 \times 10^{-6}$ Torr. Rapid thermal annealing was performed at a temperature of 600–1100°C in a N_2 atmosphere. Pulsed KrF laser annealing was performed at an energy density of 0.5–3.2 J/cm^2 in a vacuum around 2×10^{-2} Torr. The pulse length was 14 ns. The laser beam was focused onto an area of 4×4 mm^2. For each laser annealing the samples were illuminated by a single pulse unless otherwise specified. Phase transformation, the distribution of chemical species, and the microstructures of the annealed samples were examined by using transmission electron microscopy (TEM) in conjunction with energy dispersive spectrometry (EDS), which were equipped with a field emission gun with an electron probe 12 Å in size.

3. Results and discussion

3.1. Furnace annealing

For the samples annealed at a temperature of 500–600°C hexagonal $Mo(Si_{1-x}Ge_x)_2$, hereafter referred to h-$Mo(Si_{1-x}Ge_x)_2$, was formed. Above 700°C all h-$Mo(Si_{1-x}Ge_x)_2$ was transformed to tetragonal $Mo(Si_{1-x}Ge_x)_2$, hereafter referred to t-$Mo(Si_{1-x}Ge_x)_2$. From XTEM examination the $Mo(Si_{1-x}Ge_x)_2$ layers were continuous without agglomeration. From EDS analysis the Ge concentration in the $Mo(Si_{1-x}Ge_x)_2$ layer was significantly deficient with the extent becoming more severe at higher annealing temperatures. One example is shown in Fig. 1, in which Ge segregates from the h-$Mo(Si_{1-x}Ge_x)_2$ layer to the underlying $Si_{0.76}Ge_{0.24}$, forming a Ge-rich $Si_{1-x}Ge_x$ layer. In the h-$Mo(Si_{1-x}Ge_x)_2$ layer the upper part is nearly Ge-free, while the lower part contains little amounts of Ge. It is interesting to note that in Fig. 1 two isolated areas with bright contrast underlying the $Mo(Si_{1-x}Ge_x)_2$ layer are present, which even penetrate to the Si substrate. From

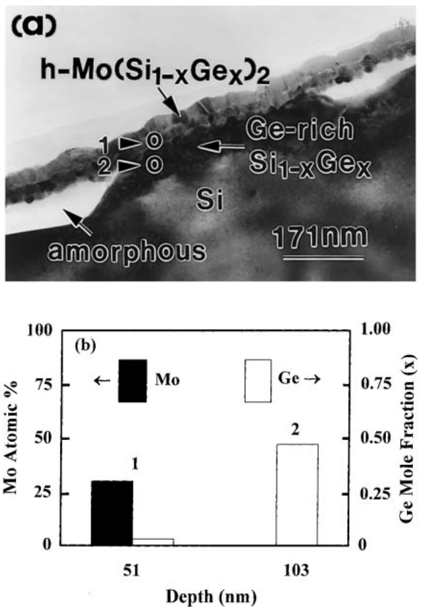

Fig. 1. (a) XTEM micrograph and (b) the depth profiles of the chemical species for the $Mo/Si_{0.76}Ge_{0.24}$ sample annealed at 550°C.

microdiffraction analysis the two areas are amorphous. Furthermore, the EDS analysis in Fig. 2 shows that the two areas are Ge-free and deficient in Si. It is well known that in the thermal reactions of Mo/Si Si is the dominant diffusion species. It seems that upon vacuum annealing Ge diffuses out of the amorphous areas to react with $Si_{0.76}Ge_{0.24}$, forming Ge-rich $Si_{1-x}Ge_x$, meanwhile Si diffuses out of them to react with the Mo overlayer, forming $MoSi_2$ and Ge-deficient $Mo(Si_{1-x}Ge_x)_2$.

In our previous studies such as Ni [4], Pd [9] and Co [16] on $Si_{0.76}Ge_{0.24}$, the agglomeration of Ge-deficient germanosilicide started to appear at a temperature of 400–500°C. However, in the present study the $Mo(Si_{1-x}Ge_x)_2$ layer remained continuous even after 700°C annealing. It is conjectured that the interfacial energy of $Mo(Si_{1-x}Ge_x)_2/Si_{1-x}Ge_x$ is significantly lower than those of Co, Ni and Pd germanosilicides on $Si_{1-x}Ge_x$.

Upon rapid thermal annealing h-$Mo(Si_{1-x}Ge_x)_2$ and t-$Mo(Si_{1-x}Ge_x)_2$ were formed at 750°C and 950°C, respectively. At 750°C, the same phenomena, i.e., Ge segregation and the formation of amorphous structures, as observed in vacuum annealing also occurred.

3.2. Pulsed laser annealing

For the samples annealed at an energy density of 0.9–1.2 J/cm^2 h-$Mo(Si_{1-x}Ge_x)_2$ was formed concurrently with significant amount of remaining Mo. At an energy density of 1.4–2.8 J/cm^2 Mo was completely transformed to h-$Mo(Si_{1-x}Ge_x)_2$ and $Mo_5(Si_{1-x}Ge_x)_3$ as shown in Fig. 3. At 2.6 J/cm^2 constitutional supercooling apparently occurred with the $Si_{1-x}Ge_x$ islands surrounded by the germanosilicide. At an energy density of 3.0–3.2 J/cm^2 $Mo_5(Si_{1-x}Ge_x)_3$ was completely transformed to h-$Mo(Si_{1-x}Ge_x)_2$. The sluggish transformation from $Mo_5(Si_{1-x}Ge_x)_3$ to h-$Mo(Si_{1-x}Ge_x)_2$ may be attributed to the rapid melt/solidification process for pulsed laser annealing, in which the reaction time is too short to allow the intermixing between the species to be complete. In addition, it is worth to note that even after annealing at 3.2 J/cm^2 t-$Mo(Si_{1-x}Ge_x)_2$ was still absent.

Upon multiple-pulse annealing pure h-$Mo(Si_{1-x}Ge_x)_2$ films can be grown at lower energy densities. In the present study, pure and continuous h-$Mo(Si_{1-x}Ge_x)_2$ films have been grown at 0.5 J/cm^2 for 50 pulses, 0.6 J/cm^2 for 30 pulses, 0.8 J/cm^2 for 20 pulses, and 1.0 J/cm^2 for 10 pulses, respectively. One example is shown in Fig. 4, in

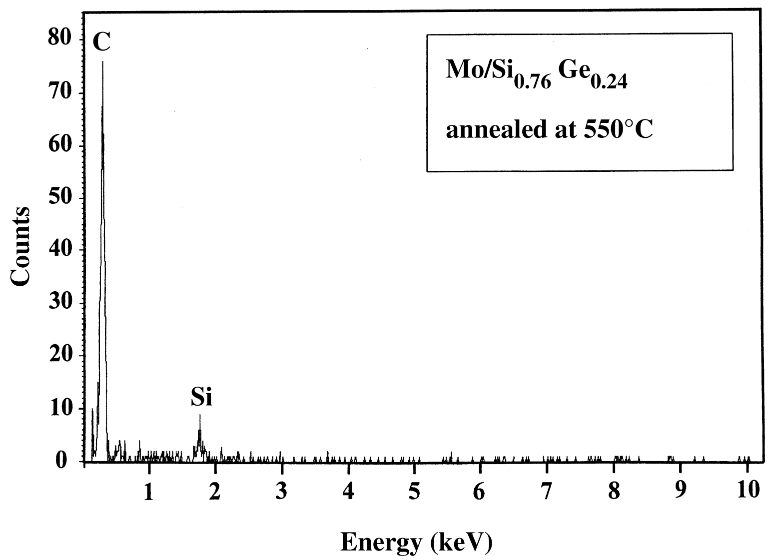

Fig. 2. EDS spectra of the amorphous structures appearing in Fig. 1(a).

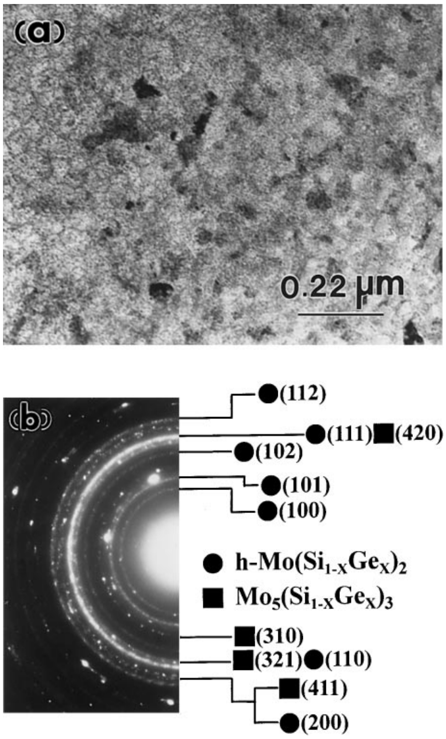

Fig. 3. (a) Plan-view micrograph of the sample annealed at 1.4 J/cm^2. (b) Electron diffraction patterns (DP) of (a) showing that h-Mo($Si_{1-x}Ge_x$)$_2$ was formed concurrently with $Mo_5(Si_{1-x}Ge_x)_3$.

which no amorphous structures appear in the $Si_{1-x}Ge_x$ film. Evidently, the microstructures of the laser-annealed samples are superior to those of the furnace-annealed samples. This result may be explained in terms of the rapid melt/solidification process for pulsed laser annealing. During pulsed laser annealing although the pulse length, 14 ns, is very short, it allows the species such as Mo, Si, and Ge to intermix between each other in the melt and then form the Mo germanosilicide in a rapid quench. The interfacial reactions can be proceeded by each individual pulse. Inversely, for furnace annealing Si and Ge are the diffusion species and the annealing time is long enough to allow them to diffuse out of the $Si_{0.76}Ge_{0.24}$ film, forming the amorphous structures as shown in Fig. 1. However, upon multiple-pulse annealing significant amounts of Ge segregation out of the germanosilicide to the underlying $Si_{0.76}Ge_{0.24}$ still occurred

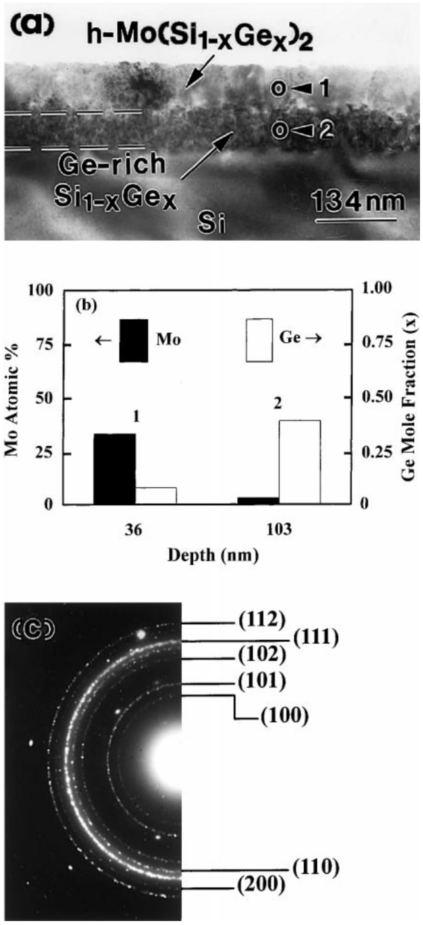

Fig. 4. (a) XTEM micrograph and (b) the depth profiles of the chemical species for the sample annealed at 1.0 J/cm^2 for 10 pulses, (c) DP of the h-Mo($Si_{1-x}Ge_x$)$_2$ layer.

as seen in Fig. 4(b). It has been found that for Pd [9] and Co [20] on $Si_{0.76}Ge_{0.24}$ multiple-pulse annealing at an appropriate energy density is an effective method to produce a continuous germanosilicide film without inducing Ge segregation to the unreacted $Si_{0.76}Ge_{0.24}$ film and strain relaxation. This discrepancy may be attributed to the larger difference between the heats of formation for $MoSi_2$, −44 kJ/mol, and $MoGe_2$, −14 kJ/mol, as compared with those for Pd_2Si, −65 kJ/mol, Pd_2Ge, −58 kJ/mol, $CoSi_2$, −33 kJ/mol, and $CoGe_2$, −12 kJ/mol [27].

In the present study, h-Mo($Si_{1-x}Ge_x$)$_2$ remained inert without transforming to t-Mo($Si_{1-x}Ge_x$)$_2$

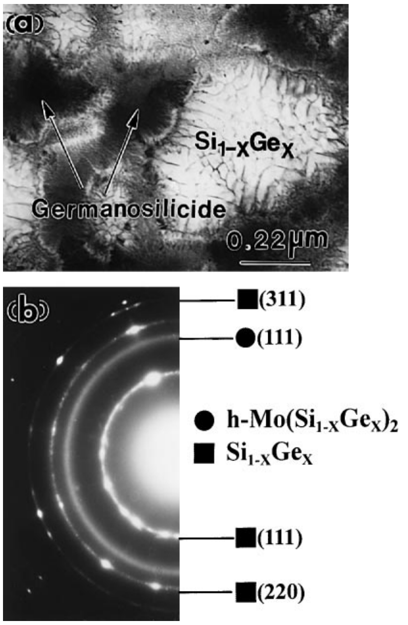

Fig. 5. (a) Plan-view micrograph of the sample annealed at 2.6 J/cm^2 for 20 pulses. (b) DP of (a) showing that h-Mo$(Si_{1-x}Ge_x)_2$ was formed concurrently with poly-$Si_{1-x}Ge_x$.

even after annealing at higher energy densities such as 3.2 J/cm^2 for one pulse and 2.6 J/cm^2 for 20 pulses. One example is shown in Fig. 5. It is conceived that during pulsed laser annealing the rapid melt/solidification process renders the reaction kinetics to play an important role in determining the phase formation. The present results indicate that the reaction kinetics favors the formation of the low temperature phase, h-Mo$(Si_{1-x}Ge_x)_2$.

4. Summary and conclusions

1. Upon conventional annealing continuous Ge-deficient Mo$(Si_{1-x}Ge_x)_2$ film was formed, while Ge-free amorphous structures appeared in the $Si_{0.76}Ge_{0.24}$ substrate. Ge segregated from the amorphous structures and the Mo$(Si_{1-x}Ge_x)_2$ film to the remaining $Si_{0.76}Ge_{0.24}$ substrate, forming Ge-rich $Si_{1-x}Ge_x$. At higher temperatures, h-Mo$(Si_{1-x}Ge_x)_2$ was transformed to t-Mo$(Si_{1-x}Ge_x)_2$.
2. Upon multiple-pulse laser annealing at an energy density of 0.5–1.0 J/cm^2 a continuous and smooth h-Mo$(Si_{1-x}Ge_x)_2$ film was formed, no amorphous structures appeared in the $Si_{0.76}Ge_{0.24}$ film. However, Ge segregation from the Mo$(Si_{1-x}Ge_x)_2$ film to the underlying $Si_{0.76}Ge_{0.24}$ film still occurred.
3. In the present study, even after annealing at higher energy densities such as 3.2 J/cm^2 for one pulse and 2.6 J/cm^2 for 20 pulses, respectively, h-Mo$(Si_{1-x}Ge_x)_2$ remained inert without transforming to t-Mo$(Si_{1-x}Ge_x)_2$. It is conjectured that the rapid melt/solidification process for pulsed laser annealing renders the reaction kinetics to favor the growth of h-Mo$(Si_{1-x}Ge_x)_2$.

References

[1] S.S. Iyer, G.L. Patton, J.M. Stork, B.S. Meyerson, D.L. Harame, IEEE. Trans. Electron. Dev. 36 (1989) 2043.
[2] R.D. Thompson, K.N. Tu, J. Angillelo, S. Delage, S.S. Iyer, J. Electrochem. Soc. 135 (1988) 3161.
[3] J.S. Luo, W.T. Lin, C.Y. Chang, W.C. Tsai, J. Appl. Phys. 82 (1997) 3621.
[4] J.S. Luo, W.T. Lin, C.Y. Chang, W.C. Tsai, Mater. Chem. Phys. 54 (1998) 160.
[5] Q.Z. Hong, J.W. Mayer, J. Appl. Phys. 66 (1989) 611.
[6] H.K. Liou, X. Wu, U. Gennser, S.S. Iyer, K.N. Tu, E.S. Yang, Appl. Phys. Lett. 60 (1992) 577.
[7] A. Buxbaum, M. Eizenberg, A. Raizman, F. Schaffler, Appl. Phys. Lett. 59 (1991) 665.
[8] A. Buxbuam, E. Zolotoyabko, M. Eizenberg, F. Schaffler, Thin Solid Films 222 (1992) 157.
[9] D.R. Chen, J.S. Luo, W.T. Lin, C.Y. Chang, P.S. Shin, Appl. Phys. Lett. 73 (1998) 1355.
[10] O. Thomas, S. Delage, F.M. d'Herule, G. Scilla, Appl. Phys. Lett. 54 (1989) 228.
[11] W.J. Oi, B.Z. Li, W.N. Huang, Z.G. Gu, H.Q. Lu, X.J. Zhang, M. Zhang, G.S. Dong, D.C. Miller, R.G. Aitken, J. Appl. Phys. 77 (1995) 1086.
[12] D.B. Aldrich, Y.L. Chen, D.E. Sayers, R.J. Nemanich, S.P. Ashburn, M.C. Ozturk, J. Appl. Phys. 77 (1995) 5107.
[13] D.B. Aldrich, H.L. Heck, Y.L. Chen, D.E. Sayers, R.J. Nemanich, J. Appl. Phys. 78 (1995) 4958.
[14] A. Eyal, R. Brener, R. Beserman, M. Eizenberg, Z. Atzmon, D.J. Smith, J.W. Mayer, Appl. Phys. Lett. 69 (1996) 64.
[15] W. Freiman, A. Eyal, Y.L. Khait, R. Beserman, K. Dettmer, Appl. Phys. Lett. 69 (1996) 3821.
[16] J.S. Luo, W.T. Lin, C.Y. Chang, W.C. Tsai, S.J. Wang, Mater. Chem. Phys. 48 (1997) 140.

[17] M.C. Ridgway, R.G. Elliman, N. Hauser, J.M. Baribeau, T.E. Jackman, Mater. Res. Soc. Symp. Proc. 260 (1992) 857.
[18] F. Lin, G. Sarcona, M.K. Hatalis, A.F. Cserhati, E. Austin, D.W. Greve, Thin Solid Films 250 (1994) 20.
[19] Z. Wang, Y.L. Chen, H. Ying, R.J. Nemanich, D.E. Sayer, Mater. Res. Soc. Symp. Proc. 320 (1994) 397.
[20] J.S. Luo, Y.L. Hang, W.T. Lin, C.Y. Chang, P.S. Shih, J. Mater. Res. 14 (1999) 3433.
[21] V. Aubry, F. Meyer, R. Laval, C. Clerc, P. Warren, D. Dutartre, Mater. Res. Soc. Symp. Proc. 320 (1994) 299.
[22] V. Aubry, F. Meyer, R. Laval, C. Clerc, P. Warren, D. Dutartre, Appl. Surf. Sci. 73 (1993) 285.
[23] Q.Z. Hong, J.W. Mayer, Mater. Res. Soc. Symp. Proc. 181 (1990) 145.
[24] E.J. Jaquez, A.E. Bair, T.L. Alford, Appl. Phys. Lett. 70 (1997) 874.
[25] J.S. Luo, W.T. Lin, C.Y. Chang, P.S. Shih, Thin Solid Films 346 (1999) 207.
[26] Z. Wang, D.B. Aldrich, R.J. Nemanich, D.E. Sayers, J. Appl. Phys. 82 (1997) 2342.
[27] F.R. Deboer, R. Boom, W.C. Mattens, A.R. Miedema, A.K. Niessen (Eds.), Cohesion in Metals: Transition Metal Alloys, North-Holland, Amsterdam, 1988.