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Raman Spectroscopic Analysis of Mo/Si Multilayers

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Raman spectra are reported from $MoSi_2$ polycrystalline powder and soft x-ray Mo/Si multilayers. The sharp lines at 323 and 438 cm^{-1} are all due to crystalline $MoSi_2$. These lines in the powder sample intensify with annealing. The Raman spectra of as-deposited multilayers shows a broad asymmetric peak, highest at about 480 cm^{-1}. We attribute this to *a*-Si which is highly disordered. In contrast to *a*-Si in semiconductor/semiconductor and semiconductor/dielectric multilayers, in the Mo/Si samples the Raman signal can vanish after modest heating. This provides evidence that the composition of the silicon component of the multilayer changes even with 200°C annealing. Further annealing also produces the signature for crystalline $MoSi_2$ in the multilayer samples. This is the first report of the characterization of Mo/Si soft x-ray multilayers by Raman spectroscopy, and it indicates that Raman spectroscopy may be an effective technique for characterizing these soft x-ray multilayers and may be useful in studying their interfaces. © 1992 Academic Press, Inc.

INTRODUCTION

Understanding the formation of refractor metal silicides at the interfaces of thin films is an extremely interesting basic science and an important technological problem. Technologically, the formation of silicide is important in very large-scale integration (VLSI) where silicides are being used as interconnect films (*1, 2*) and in producing better soft x-ray multilayers, since their presence at interfaces in real Mo/Si multilayers keeps the peak reflectance from achieving the theoretical maximum of 80% which is predicted for multilayers containing atomically abrupt and smooth interfaces.

Besides their applications in x-ray imaging technology and microelectronics, multilayers have also proven to be a convenient way of studying the nanoscale properties of materials—for example, the crystallization and interdiffusion of matter on atomic scales (*3, 4*).

In the current x-ray imaging revolution periodic bilayer multilayers have played an important role (*5*). These multilayer mirrors, which are used to reflect light with the wavelengths in soft x rays, typically consist of periodic multiple bilayers, each bilayer composed of a low-Z and a high-Z layer. The reflectance is achieved by the interference occurring at the sharp interfaces between these layers. Generally speaking, the sharper the interfaces, the higher the reflectance which can be obtained. Any modification of the interfaces will directly impact the optical performance of the multilayer. Techniques

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which can detect and quantify the intermixing at interfaces are extremely important for preparing the superior multilayers required for soft x-ray projection lithography, since at 10 percentage point gain in the reflectance in each of the mirrors of the eight-mirror systems contemplated for lithography can triple the light through the camera.

Small angle x-ray diffraction (SAXRD) and direct imaging by scanning transmission electron microscopy (STEM) have been successful in characterizing interfaces of soft x-ray multilayers but can give artificially wide estimates of interfaces. Raman spectroscopy has also been shown to be a useful technique for characterizing multilayers of amorphous semiconductors, such as Si/Ge (*6*), and multilayers of metal/carbon, such as W/C multilayers (*7*) because it can directly "count" interfacial bands in some cases. Observing the interfaces of the multilayers is especially important, but under some circumstances this is very difficult and may require special care. This is because of the small volume of material within the interfaces and the interface bonds may have a low Raman cross section.

So far, Mo/Si is the most efficient multilayer mirror for the soft x-ray range of 13–30 nm (*8–11*). A large number of groups are studying these multilayers and their applications because of the high theoretical and achieved peak reflectances of 80% and 65%, respectively, over the 12.5 to 16 nm range. This is the preferred range for projection soft x-ray lithography. We are the first group to apply a Raman spectroscopic technique to characterize soft x-ray Mo/Si multilayers. We have observed the presence of *a*-Si in as-deposited multilayers and its disappearance and the formation of crystalline $MoSi_2$ in annealed multilayers. The Raman spectroscopy study of commercial $MoSi_2$ powder has also been carried out to help identify the $MoSi_2$ peaks.

EXPERIMENTAL

The multilayer interfacial regions consist of a mixture of molybdenum and silicon, so that the study of molybdenum silicide is required for Raman studies of Mo/Si multilayers and we began with a study of molybdenum disilicide ($MoSi_2$) powder. For this reason, this study of multilayers has applications beyond the study of soft x-ray reflectors since silicides are expected to be important materials for high-speed electronics and very large-scale integration (VLSI). This is because many refractory metal silicides have been found to have very high thermal and chemical stability and high electrical conductivity. Because of these applications, silicides have received substantial attention, and a large number of studies have been carried out on them (*1, 2*). Many silicides such as WSi_2, PtSi, and $TiSi_2$ have been extensively studied by Raman spectroscopy (*12–18*), but there has only been one published report on $MoSi_2$ (*19*).

The molybdenum disilicide powder was purchased from Aldrich Chemical Company, Inc. The powder's average particle size is about 1 μm and its manufacturer quotes the purity as 99^{+}%. The bulk material was obtained to provide a standard with which to compare the thin film material.

In addition to studying the as-received $MoSi_2$ powder and the as-deposited thin film samples, both powder and films were subjected to vacuum and to air annealing, and the powder to KOH etching. This was done to aid understanding of the observed features in Raman and x-ray diffraction spectra. The vacuum annealing consisted of sealing the sample in an evacuated quartz tube or glass ampoule. For the sample annealed in air, the ampoule was not sealed. The furnace was controlled to 1000°C

and the sample was placed directly in the hot oven at the beginning of the annealing time and air quenched by withdrawing the ampoule directly from the furnace at the end of the annealing time. As an alternative to annealing and to etch out the unreacted materials and impurities, some of the powder was mixed with KOH solution (10 *M* KOH), filtered, and dried in air in a 110°C oven. This etching process was observed to remove most of the residual unreacted silicon.

The multilayer samples were made by dc magnetron sputtering for a fixed target system. Layering was achieved by rotating the substrate in the system over the sources at a fixed rate. The Mo/Si multilayers were prepared for soft x-ray mirror (plasma diagnostic) applications and were shown to have excellent soft x-ray reflectance. The sputtering targets were molybdenum metal and *p*-type silicon. The sample substrates were ultrasmooth crystalline silicon wafers of [100] orientation. The period Λ or *d*-spacing was measured to be 8.4 nm, as deposited, with a nominal $\gamma = d_{Mo}/(d_{Si} + d_{Mo})$ of 0.40. There were 30 pairs. The total multilayer thickness is thus about 250 nm. The top layer is amorphous silicon and is twice as thick as other layers to retard oxidation. The multilayer samples were also sealed in vacuum and annealed at temperatures ranging from 300 to 1000°C.

The Raman spectra were recorded on a SPEX 1877 Triplemate spectrometer. The spectrometer consists of a modified Czerny–Turner zero-dispersion double spectrometer as a filter stage and a modified Czerny–Turner spectrograph. The dispersion element used in the spectrograph stage is a 1800 groove/mm holographic grating with 0.92 nm/mm dispersion. The spectral bandpass selected was $\sim$18 cm^{-1}. The 514.5-nm line ($\sim$400 mW) of an argon ion laser (LEXEL 96) was used as the excitation source in most studies. The other laser lines were used on occasion to confirm peak identification. A 1200 groove/mm ruled grating with a small aperture placed outside of the laser cavity was used as a presample monochromator to eliminate the laser plasma lines. The laser beam was brought to line focus (1 $\times$ 10 mm) on the sample's surface using a cylindrical lens to match the entrance slit of the triplemate monochromator; the scattered signals were analyzed by the spectrometer and detected by a photomultiplier (EMI 7981B). Then photon-counting electronics were used to convert the light signal into the electrical signal. A 386SX PC was used to control the spectral scanning and data acquisition through a digital–analog interface box (TransEra-MDAS-7000).

RESULTS AND DISCUSSION

The Raman spectra of the commercial molybdenum disilicide powder samples are shown in Fig. 1. The raw powder (as-received) spectrum (see (a)) has four peaks: two small broad peaks located at 323 and 438 cm^{-1} (the higher frequency one is stronger), one fairly sharp peak located at 520 cm^{-1}, and one small peak located at 822 cm^{-1}. We conclude that the sharp peak at 520 cm^{-1} arises from the nonreacted polycrystalline silicon in the powder. This is suggested by its position and was confirmed by two observations; first, that the 520 cm^{-1} peak is lower after vacuum annealing at 1000°C (see (b)), and, second, that it is entirely absent after etching in KOH (see (c)). Strong alkali will etch crystalline silicon but will not etch $MoSi_2$. Other investigators have also reported the presence of unreacted silicon in as-received silicide powders (*12, 16*). We conclude that the high-frequency peak is due to MoO_3 impurity. This was suspected

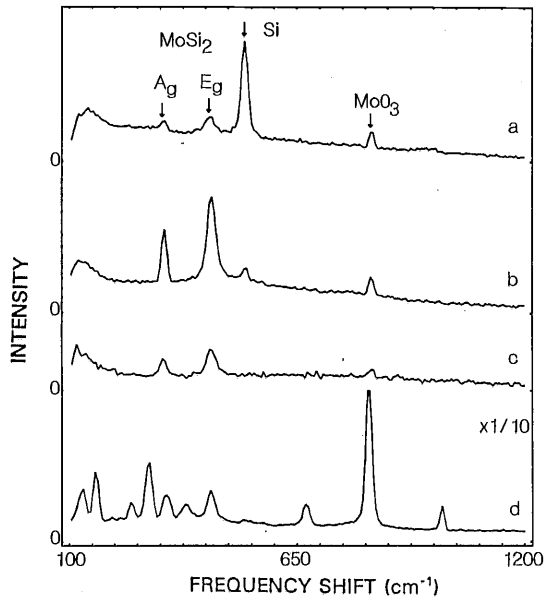

FIG. 1. Raman spectra of $MoSi_2$ powder: (a) as-received, (c) etched in 10 *M* KOH and dried in air, (b) annealed in vacuum at 1000°C for 1 h, (d) annealed in air at 500°C for 1 h.

because of the position of the line and was confirmed by annealing in air (see (d)), as will be discussed below. The two low-frequency peaks are due to $MoSi_2$. Doland and Nemanich (*19*) recently reported the position of $MoSi_2$ prepared by annealing Mo on Si wafers as being 325 and 440 cm^{-1}, which are close to our measurements of 323 and 438 cm^{-1}. These peaks are also close to those of WSi_2 at 331 and 451 cm^{-1} (*12*), which has been studied more extensively (*12–16*).

After the powder sample was annealed in vacuum at 1000°C for 1 h, we saw that the two $MoSi_2$ peaks became sharper and stronger (see (b)). This can be interpreted as meaning that during the annealing process the original small grains of crystalline $MoSi_2$ grew into larger grains which possess a larger Raman cross section. Analogous behavior, grain growth with concurrent sharpening and growth of the Raman signal, has been seen in the annealing of amorphous and microcrystalline Si. Note that even after annealing the 520 cm^{-1} peak is still observable though smaller. We interpret this decrease in the silicon peak intensity as the partial reaction of some of the unreacted silicon during annealing.

To test the hypothesis that the 822 cm^{-1} peak is due to MoO_3 we annealed the same sample again in air at 500°C for 1 h. The peak became more intense (see (d)). Note that in concert with the intensification many other weak peaks also appear. Their positions are 996, 665, 438, 374, 329, 286, 245, 218, 199, 159, and 129 cm^{-1}. Because the purpose of this experiment was only to verify that the peak at 822 cm^{-1} is from MoO_3, the resolution was not optimized. This led to the undistinguishable peaks at 374 and 329 cm^{-1}. Jeziorowski and Knözinger reported peaks at 380, 367, 337, and 292 cm^{-1} (*20*). They also reported another peak at 117 cm^{-1} which we identify as an

Ar^+ laser plasma line. We have seen this line regardless of the sample we used. The aperture of the plasma-line eliminator is not sufficiently narrow to completely eliminate plasma lines near the elastically scattered laser light. Excluding this 117 cm^{-1} line and the $MoSi_2$ signal, curve (d) represents a perfect Raman spectrum of MoO_3 (*20–22*). The 338 cm^{-1} peak has been covered by the stronger MoO_3 signal. In traces (a) and (b) the oxide impurity was too small to produce a large Raman signal, and only the strongest peak of the oxide was observed. In (b), because the powder was annealed in vacuum, there is no way for oxide to be removed, so the oxide's signal remains.

Raman spectra from Mo/Si multilayers are shown in Fig. 2. The spectrum of the as-prepared multilayer sample only gives a broad bump located approximately at 480 cm^{-1} (see Fig. 2a). We attribute this feature to amorphous silicon (*23*). The silicon layers of Mo/Si multilayers have previously been reported to be amorphous on the basis of transmission electron microscopy (*24*). Curve (a) provides direct evidence that these layers are amorphous and, furthermore, indicates that the amorphous silicon is highly defective since the peak is broad and weak. The metallic layers generally do not produce strong Raman signals and we see no evidence of them. We also do not see evidence of Mo–Si bonds in the as-deposited multilayers.

We subjected our sample to successively higher temperature vacuum annealings starting at 200°C and eventually reaching 1000°C. The amorphous silicon peak disappears at about 300°C (see (b)) and no other changes are seen until 1000°C. Curve (c) of Fig. 2 shows the Raman spectra after the sample's final vacuum annealing at 1000°C. The disappearance of the Raman peak due to amorphous silicon is noteworthy since it is opposite to what is often observed with the annealing of thicker layers of room-temperature deposited amorphous silicon. This can produce a better bonded or structurally more perfect anneal-stable amorphous silicon, possessing a Raman spectrum which is more intense and shows two humps, one centered at about 480 cm^{-1} and the other one at 170 cm^{-1}. The intensity of the peaks typically increases and the

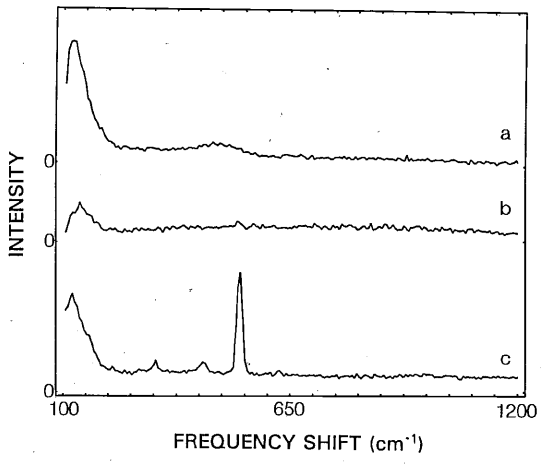

FIG. 2. The Raman spectra of a Mo/Si multilayer: (a) as prepared, (b) annealed in vacuum at 300°C for 1 h, (c) annealed in vacuum at 1000°C for 1 h.

peaks narrow with annealing (*23*). The fact that this same phenomenon does not occur for the metal/silicon samples indicates that annealing may produce *significantly different changes* in them on an atomic level than it does in pure silicon films and silicon/dielectric multilayers. The loss of signal indicates that the Raman cross section of the silicon layers has decreased. It may be that the material is becoming more defective—perhaps because metal atoms are diffusing into the silicon.

After this 1000°C annealing three peaks were seen: two peaks at 323 and 438 cm^{-1}, respectively, which can be attributed to crystalline $MoSi_2$, and one peak at 520 cm^{-1}, which can be attributed to crystalline silicon.

We believe that the appearance of molybdenum silicide peaks means that extensive interdiffusion has occurred and that in the interdiffusion region crystallization has begun, and that the crystallites formed are thick enough to produce detectable Raman signals. The annealing process may have produced a portion of the silicon component of multilayer crystalline. There is some possibility of the 520 cm^{-1} peak coming from the substrate through the film. The 250 nm thickness of the multilayer is sufficient to block any Raman emissions from the substrate in the as-deposited film. Interdiffusion and reaction at 1000°C may have made the film more transparent at the laser's 514 nm line, however. The ratio of the amplitude of the 520 cm^{-1} peak to the $MoSi_2$ peaks does not vary as the sample's position is changed. If it were due to pinholes it would vary. We have also inspected the sample's surface for cracks or pinholes that would give the laser probe access to the substrate. After annealing, the sample surface is rough on the scale of 100 nm, and we conclude that this roughening could cause thin spots that give the light access to the substrate.

Raman spectroscopy may prove to be a useful and new method of characterizing Mo/Si multilayers. It has been reported that under 600°C annealing Mo layers transform completely into polycrystalline mixtures of Mo_5Si_3 and $MoSi_2$ in both the hexagonal and the tetragonal phases (*11*). We have not seen the appearance of any molybdenum silicide until after the 1000°C annealing, and only tetragonal silicide has been obtained at that temperature. Further annealing studies may be required to see the hexagonal phase by Raman spectroscopy.

CONCLUSIONS

The Raman spectroscopy technique has been used to study polycrystalline $MoSi_2$ powder and characterize the as-prepared and annealed Mo/Si soft x-ray multilayer mirrors. The two active Raman modes of $MoSi_2$ located at 323 and 438 cm^{-1} have been observed in powder $MoSi_2$ and in annealed Mo/Si multilayers. The observation of the signal due to amorphous silicon in as-deposited multilayers and its loss later with relatively modest heating indicates that significant atomic reordering occurs at relatively modest temperatures. This observation and the observation of $MoSi_2$ in the annealed multilayer indicate that Raman spectroscopy can be a useful technique in characterizing Mo/Si multilayers and studying their interfaces.

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REFERENCES

1. T. P. CHOW AND A. J. STECKL, *IEEE Trans. Electron Devices* **ED-30,** 1480 (1983).
2. S. P. MURARKA, "Silicides for VLSI Applications," Academic Press, New York, 1983.
3. A. L. GREER AND F. SPAEPAN, *in* "Synthetic Modulated Structures" (L. Chang and B. C. Giessen, Eds.), p. 419, Academic Press, New York, 1988.
4. J. GONZALEZ-HERNANDEZ, D. D. ALLRED, AND O. V. NGUYEN, *in* "Interfaces, Superlattices, and Thin Films" (J. D. Dow and I. K. Schuller, Eds.), Material Research Society Proceedings, Vol. 77, p. 665, Pittsburgh, 1987.
5. N. M. CEGLIO, *J. X-Ray Sci. Technol.* **1,** 7 (1989).
6. D. D. ALLRED, J. GONZALEZ-HERNANDEZ, O. V. NGUYEN, D. MARTIN, AND D. PAWLIK, *J. Mater. Res.* **1,** 468 (1986).
7. D. D. ALLRED, Q. WANG, AND J. GONZALEZ-HERNANDEZ, *Mater. Res. Soc. Proc.* **160,** 605 (1990).
8. T. W. BARBEE, JR., S. MROWKA, AND M. C. HETTRICK, *Appl. Opt.* **24,** 883 (1985).
9. K. HOLLOWAY, K. B. DO, AND R. SINCLAIR, *J. Appl. Phys.* **65,** 474 (1989).
10. D. G. STEARNS, M. B. STEARNS, Y. CHENG, J. H. STITH, AND N. M. CEGLIO, *J. Phys.* **67,** 2415 (1990).
11. D. G. STEARNS, R. S. ROSEN, AND S. P. VERNON, *J. Vac. Sci. Technol. A* **9,** 2662 (1991).
12. P. J. CODELLA, F. ADAR, AND Y. S. LIU, *Appl. Phys. Lett.* **46,** 1076 (1985).
13. S. KUMAR, S. DASGUPTA, H. E. JACKSON, AND J. T. BOYD, *Appl. Phys. Lett.* **50,** 323 (1987).
14. C. CHEN, M. CAO, AND W. HUA, *J. Appl. Sci.* **9,** 258 (1991).
15. M. AMIOTTI, E. BELLANDI, A. BORGHESI, A. PIAGGI, G. GUIZZETTI, F. NAVA, AND G. QUEIROLO, *Appl. Phys. A* **54,** 181 (1992).
16. D. SUN, Z. YU, AND F. LI, *Acta Opt. Sin.* **5,** 310 (1985).
17. R. J. NEMANICH, M. J. THOMPSON, W. B. JACKSON, C. C. TSAI, AND B. L. STAFFORD, *J. Vac. Sci. Technol. B* **1,** 519 (1983).
18. R. J. NEMANICH, R. T. FULKS, B. L. STAFFORD, AND H. A. VANDER PLAS, *Appl. Phys. Lett.* **46,** 670 (1985).
19. C. M. DOLAND AND R. J. NEMANICH, *J. Mater. Res.* **5,** 2854 (1990).
20. H. JEZIOROWSKI AND H. KNÖZINGER, *J. Phys. Chem.* **84,** 1825 (1980).
21. A. N. DESIKAN, L. HUANG, AND S. T. OYAMA, *J. Phys. Chem.* **95,** 10050 (1991).
22. L. RODRIGO, K. MARCINKOWSKA, A. ADNOT, P. C. ROBERGE, S. KALIAGUINE, J. M. STENCEL, L. E. MAKOVSKY, AND J. R. DIEHL, *J. Phys. Chem.* **90,** 2690 (1986).
23. J. E. SMITH, JR., M. H. BRODSKY, B. L. CROWDER, AND M. I. NATHAN, *Phys. Rev. Lett.* **15,** 642 (1971).
24. D. G. STEARNS, R. S. ROSEN, AND S. P. VERNON, *SPIE* **1547,** 2 (1991).