*Paper*

# Growth Modes of Ba on Mo(110) Substrate

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The growth modes of Ba deposited on a Mo (110) substrate have been investigated by using reflection high-energy electron diffraction (RHEED) and scanning electron microscopy (SEM). In this study, the RHEED specular beam intensity oscillations apparatus is employed to confirm the surface flatness of thin Ba layers on Mo(110) substrate. Ba grows on the Mo(110) substrate via the Stranski-Krastanov growth mode in the temperature range between 300 and 550 °C, in which a monolayer with a (1.5×1.8) structure grows initially, followed by the growth of Ba islands with the $(111)_{Ba}$ plane. Between room temperature (R.T.) and 300 °C, Ba grows on the Mo(110) substrate via the Frank-van der Merwe growth mode, however only several periods of RHEED specular beam intensity oscillations could be observed. Such results suggest that several flat Ba layers grew on Mo(110) substrate via Frank-van der Merwe growth mode and Ba layers have much difficulty in keeping the surface flatness on a Mo(110) substrate. In the temperature range from 300 to 550 °C, only single oscillation was observed, suggesting that the Ba/Mo(110) system adopts the Stranski-Krastanov growth mode at such temperatures with the (1.5×1.8) monolayer.

## 1. Introduction

Lots of investigations regarding the growth modes of metal/metal systems have been carried out in the past [1-8]. Up to date, two types of growth modes have been confirmed such as the Frank-van der Merwe growth mode in room temperature (R.T.) region and the Stranski-Krastanov growth mode in high temperature region for thin metallic films on Mo(110) or W(110) substrates. Most research studies have dealt with ultrathin films of face centered cubic (f.c.c.) metals on the substrates of body centered cubic (b.c.c.) metals, however several studies on the growth modes of metallic b.c.c./b.c.c. systems have also been performed [9-11]. RHEED specular beam intensity oscillations have come to be an important reliable process tool for controlling the film thickness and the surface flatness mainly for semiconductor materials [12-16]. Also, several reports indicate that the RHEED specular beam intensity oscillations were succeeded in observing the ideal layer-by-layer growth even in case of metal/metal systems with different lattice structures [17-20]. However, no study has been performed with the usage of the RHEED specular beam intensity oscillations to examine growth modes of the Ba/Mo(110) system, even such results benefit lots of information on the surface flatness of thin Ba films. In this paper, the detailed information on the growth modes of Ba/Mo(110) system is drawn as a function of substrate temperature.

## 2. Experimental

The RHEED experiments were performed in an ultra-high vacuum (UHV) chamber with a base pressure of $1\times10^{-10}$ Torr. A Mo single crystal with a (110) plane whose misorientation was kept less than 0.05° was used as a substrate. Details of the experimental procedures are described elsewhere [21-24]. The Mo substrate was cleaned by annealing at 700 °C under an oxygen atmosphere of $1\times10^{-6}$ Torr for 10 min followed by flash annealing at 1600 °C in a vacuum of $10^{-10}$ Torr for 10 sec. Based on this procedure, the clean Mo(110) substrate was obtained. Ba was deposited on the clean Mo(110) substrate by heating a Ba dispenser (SAES Getters Co.). The pressure during deposition was $1\times10^{-9}$ Torr. The deposition rate and the film thickness were monitored by using a quartz oscillator. In order to examine the growth mode in detail, the Ba depositant thickness was changed

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from 0.1ML to 20ML and the substrate temperature was varied from room temperature to 900 °C. The acceleration voltage of the RHEED was kept at 20kV. To monitor the growth modes of the Ba/Mo(110) system, we observed the RHEED patterns and the RHEED specular beam intensity oscillations at various substrate temperatures. In order to observe the RHEED specular beam intensity oscillations, a charge coupled device (CCD) camera connected to a computer was employed. For the aim of confirming the configuration of Ba islands, an FE-SEM (Hitachi S-4700) was employed after removing the sample from the UHV chamber.

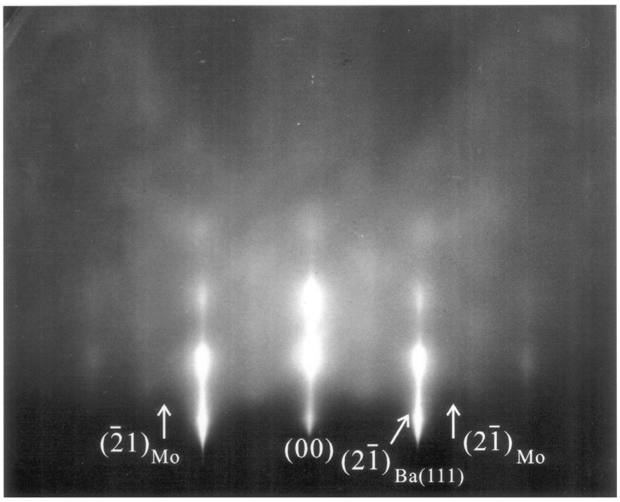


Fig.1. RHEED pattern of the specimen deposited with Ba at 4 ML at R.T.

### 3. Results and Discussion

Fig. 1 shows a RHEED pattern of the specimen after 4 ML deposition at R.T. The incident electron beam was parallel to the $[\bar{1}10]_{Mo}$ direction. With increasing the film thickness, the RHEED pattern so as to Fig. 1 grew in intensity, while the RHEED pattern originated from the (1.5×1.8) structure faded and disappeared in case above a Ba thickness of 1.5 ML. At the thickness with 4 ML, the Mo fundamental rods could not be observed except 00, suggesting that the entire surface area of Mo substrate were covered by Ba layers. In Fig. 1, each arrows with the notations $(2\bar{1})_{Mo}$ and $(\bar{2}1)_{Mo}$ indicate the actual places for Mo fundamental rods. The streak marked as $(2\bar{1})_{Ba(111)}$ was caused by Ba(111) plane.

The RHEED specular beam intensity oscillations measured along the $[\bar{1}10]_{Mo}$ direction at R.T. are represented in Fig. 2(a). To observe RHEED oscillations under the fine experimental condition, the specular beam path was arranged to be most sensitive to surface wave resonance by controlling mutual geometric relationships among the specular beam, direct beam and surface wave resonance. Resultantly, we could observe only two periods of RHEED oscillations. In the process of the first oscillation, the continuous change of RHEED patterns occurred from the clean Mo(110) substrate to the (1.5×1.8) structure via c(2×2), (1.6×2) structures. When the intensity was recovered firstly, the RHEED pattern of the (1.5×1.8) structure was most developed. In addition, the RHEED patterns of both c(2×2) and (1.6×2) structures are already shown in our previous reports [9-11]. Such results include following features concerning the growth mechanism of Ba films on a Mo(110) substrate at R.T. Ba films grow by the layer-by-layer growth mode on Mo(110) substrate at R.T.

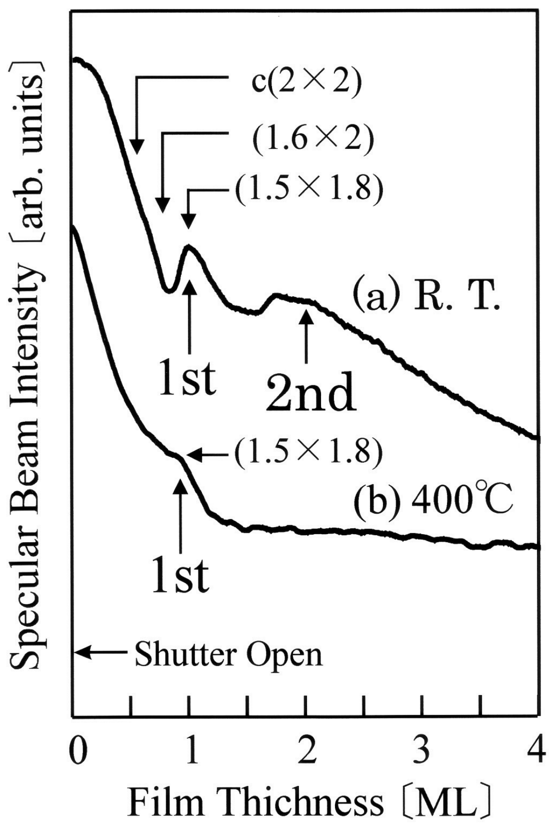


Fig.2. (a) RHEED specular beam intensity oscillations at R.T. During the first oscillation, RHEED patterns of the c(2×2), (1.6×2) and (1.5×1.8) structures appeared. (b) RHEED specular beam intensity oscillation at 400°C.

It is interesting that the Ba layers favor the hexagonal structure on Mo(110) substrate except the first monolayer with (1.5×1.8) structure, even the Ba bulk keeps the b.c.c. structure under standard condition. A high pressure X-ray diffraction studies on Ba indicate that Ba bulk crystals favor the hexagonal close packed structure above ca. $6\times10^8$ Pa [25]. The formation of Ba films on a Mo(110) substrate is match for such pressure-induced phase changes. However, the surface of the $(111)_{Ba}$ layer could not keep the surface flatness and the surface roughness easily occurred in the thickness range above 2ML, such interpretation could be done based on the experimental verification of only two periods of RHEED specular beam intensity oscillations at R.T. The atomic arrangement of the (1.5×1.8) structure is different from that of the $(111)_{Ba}$ layer, and the (1.5×1.8) structure acts as the buffer-layer of the Ba-Mo(110) interface for the smooth epitaxial growth of the $(111)_{Ba}$ layers. Resultantly, the $(111)_{Ba}$ plane can keep the following epitaxial orientation relationships thanks to the existence of the (1.5×1.8) buffer layer; $[\bar{1}10]_{Ba}//[001]_{Mo}$, $(111)_{Ba}//(110)_{Mo}$.

In many cases of the semiconductor/semiconductor systems at R.T., the experiments of RHEED specular beam intensity oscillations indicate that it is possible to form several tenth flat layers by layer-by-layer growth. In case of metal/metal systems, however, no more than several periods of the RHEED specular beam intensity oscillations can be observed, which indicates that metal/metal systems have a strong tendency to lose the surface flatness when the film thickness is greater than several monolayers at R.T. Dentel et al. described that the change of RHEED specular beam intensity oscillations in case the deposition rate is decreased is similar to the change observed while temperature is increased. Such valuable explanation deduce a conclusion that the surface diffusion length is increased either by decreasing the deposition rate or by increasing the temperature. So, the formation of several tenth flat layers of metals on metal substrates needs higher deposition rates or lower substrate temperatures. Moreover, based on the comparison with Nd layers on Mo(110) substrate [24], Ba may have longer surface diffusion length than that of Nd at the same temperature, so it seems to be difficult to form so flat surface with Ba layers at R.T. On the other hand, the experimental result of the RHEED specular beam intensity oscillations at 400°C is indicated in Fig. 2 (b). Only single period of oscillation was observed in the temperature range from 300 to 550 °C, suggesting that the completion of the first monoatomic layer with the (1.5×1.8) structure occurred during single oscillation via the appearance of the c(2×2) and (1.6×2) structures. Such result supports the island growth on a monolayer for Ba/Mo(110) system in relatively high temperature region.

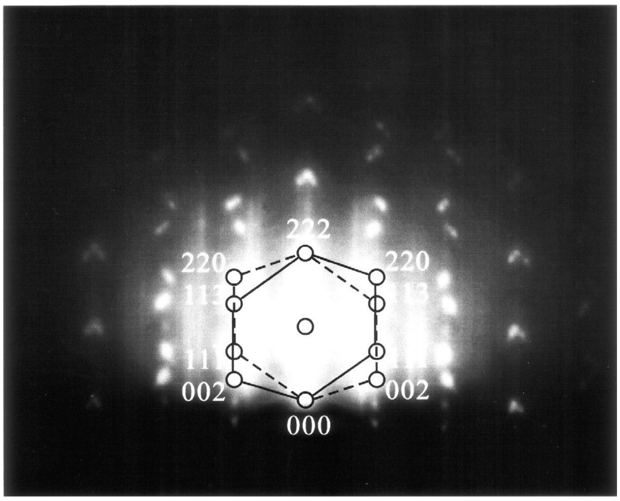


Fig. 3. RHEED pattern of the specimen deposited with Ba at 4 ML at 400 °C.

Fig. 3 shows a RHEED pattern of a 4ML-thick Ba film deposited at the substrate temperature of 400 °C. In contrast to the RHEED pattern in Fig. 1 which was obtained at R.T., the fundamental Mo rods, the streaks due to both the (1.5×1.8) and $(111)_{Ba}$, and the multiple scattering spots are visible at the same time. Such RHEED pattern is maintained as the deposition thickness increases at relatively high temperature region. The result of this RHEED observation suggests that three-dimensional Ba islands grow after the completion of the first (1.5×1.8) monolayer. Especially, the intensity of transmitted spots through Ba islands is very high. So, the occurrence of the sufficient surface diffusion of Ba adatoms effectively contributed to the island formations. Because of the existence of both twin Ba crystals and Ba crystals with the symmetric atomic arrangements along the $[001]_{Mo}$ axis, the coordination of diffracted spots is symmetric with respect to the $[111]_{Mo}$ axis. Two sets of the spots 000, 111, 222, 002, $1\bar{1}1$, 113, and 220 are inversely indicated on the RHEED pattern in Fig. 3. Each hexagons connected by straight lines and by dotted lines indicate each sets of diffracted spots due to both twin Ba crystals and Ba crystals with the symmetric atomic arrangements along the $[001]_{Mo}$ axis. The spots clearly indicate that the crystal structure of Ba islands on the Mo(110) substrate never adopts the b.c.c., but f.c.c. structure. Fig. 4 shows a SEM image of the specimen with a 4ML-thick Ba film at 400 °C. The diameter of the islands is ca. 200 nm. In this study, observed Ba islands showed the round-like configuration, not similar to Pb and Nd islands with the hexagonal shapes [1, 24], however RHEED results suggests that Ba islands are expected to favor triangle or hexagonal faceted shapes.

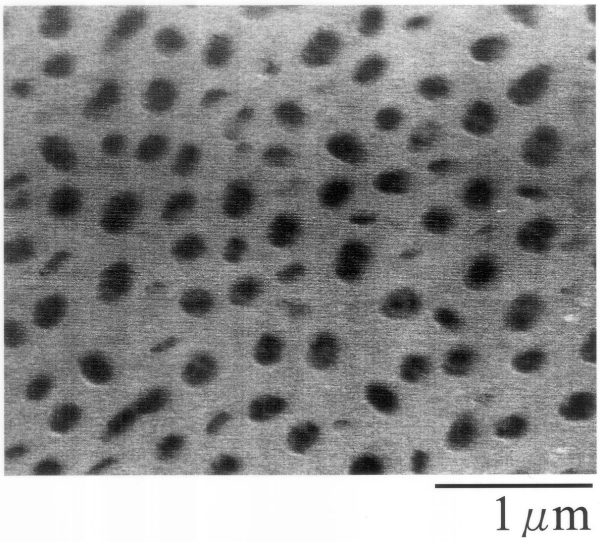


Fig. 4. SEM image of the specimen with a 4ML-thick Ba film at 400 °C.

**4. Conclusion**

The growth modes of Ba deposited on a Mo(110) substrate at various substrate temperatures have been investigated in this study. At R.T., Ba grows on a Mo(110) substrate in accordance with the Frank-van der Merwe growth mode, however thin Ba layers possess a strong tendency to lose the surface flatness on Mo(110) substrate. In the temperature range between 300 and 550 °C, Ba grows on a Mo(110) substrate in accordance with the Stranski-Krastanov growth mode. The Ba islands kept their diameter with ca. 200 nm in this study.

**5. Acknowledgements**

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査読コメント

**査読者 1.** 中原　仁（名古屋大学）

本論文は、これまでに報告例のない Ba on Mo(110) の薄膜成長を反射高速電子回折と走査電子顕微鏡で調べたものであり、metal film on metal 系の成長メカニズムに新たな情報を与えるものである。

従って、本論文は掲載可と判断するが、以下に示した説明が不十分を思われる点を追加した方が望ましい。

**[査読者 1-1]**

おそらく SEM 観察は ex-situ で行っているものと思われますが、そうであれば Experimental でその点を明示してください。

**[著者]**

ご指摘のとおり、ex-situ による観察結果です。Experimental に加筆致しました。

**[査読者 1-2]**

Fig.3 の RHEED 図形には、明瞭なファセットからの回折が見えています(逆 V 字、或は斜めに伸びたスポット)。このことは成長した島の形状が特定のファセットで囲まれた形状(おそらくは三角形あるいは六角形)をしていることを強く示唆します。しかし一方で、SEM 像では明瞭なファセットの存在は観察されていません。

本文では、SEM の結果から Ba は Pb や Nd と異なって島の形状は丸いとしていますが、SEM 観察の際に試料を UHV から大気に取り出したとき酸化などの反応によって島の形状変化が起こっている可能性が考えられます。

SEM 観察後に再び RHEED 観察を行い、大気暴露の影響の有無を確認した上で、考察を加えた方がよいと思います。

**[著者]**

ご指摘のとおり、RHEED 図形と SEM 観察の結果との間に論理的に整合しない点があります。この点に関して今後充分な実験を実施した上で解釈を行う必要があると判断致しました。従いまして、島の形態については、従来の解釈を削除すると共に、#1 本実験で SEM 観察された島は丸みを帯びたものであったという事実説明、#2 RHEED 図形からは本来六角形もしくは三角形の明瞭なファセットを示す島の形成が期待されるとの説明を加えました。

**査読者 2.** 井上　雅彦（摂南大学）

本論文は、著者らがこれまで RHEED を用いて系統的に研究を行ってきた Ba/Mo(110)系 のエピタキシャル成長様式の研究に連なるもので、RHEED スポット強度振動の観察結果から著者らの従来のモデルを傍証しており、JSA に掲載する価値があるものと判断します。

論文をよりクリヤにするため、以下の点を修正あるいは追加すべきと思いますのでご検討ください。

**[査読者 2-1]**

Fig.1 で、（見えてはいないものの）Mo(110)からの基本ロッドの位置を矢印などで示した方が基板が完全に覆われていることがハッキリして良いと思います。

また、見えているストリークが Ba(111）からの基本反射であることを示し、主なところに index をつけた方が良いと思います。

**[著者]**

Fig. 1 を [110]Mo 入射の RHEED 像に差替えた上で、本来観察されるべき Mo 基本ロッド位置に index を示し本文に説明を加えました。また、Ba(111)に起因するストリークの一つに index を示しました。

**[査読者 2-2]**

Fig.1 の入射方位は、Fig.3 と比較するために [001]Mo としたとあります。しかし、強度振動を測定した Fig.2 では [011]Mo 入射ですので、Fig.1 では [011]Mo 入射で、強度振動を測定したときと同じ入射角の RHEED 写真を示し、鏡面反射スポットが３次元回折の影響を受けていないこととか、表面波共鳴条件を使って、二次元構造に敏感な条件で測定していることなど(そうされたかどうか不明ですが)を写真と文章で示された方が良いと思います。

そして従来の Fig.1 をもし残すなら Fig.3 の直前に並べてはいかがでしょうか。

本論文は強度振動の測定がメインの内容なのですから、上記のように強度振動測定に関連する情報を示す RHEED 写真を配置すべきと思いました。

**[著者]**

Fig. 1 を[110]Mo 方位の RHEED 像に変更しました。

また、[001]Mo 方位の RHEED 像の情報は、Fig.3 に重畳的に観察されますので残す意味は薄いと判断し、その相違を文章で説明するにとどめ、削除致しました。また、鏡面反射スポットが 3 次元回折の影響を受けていないこと、表面波共鳴条件を用いて 2 次元構造に敏感な条件で測定を実施したことは確かですので、このことを文章に加えました。ダイレクトビーム，鏡面反射点，表面波共鳴線それぞれの位置関係が判る RHEED 像を示すべきだと思いましたが、清浄表面時に明瞭であったそれぞれの強度自体が膜厚増加と共に大幅に減衰し、証拠として提示できる写真の取得自体が困難でした。従いまして、文章で説明するのみにとどめることと致しました。Ba/Mo(110)系に於いては半導体と異なり、RHEED 振動のデータ取得それ自体が困難であることを斟酌して頂けますと幸甚です。

**[査読者 2-3]**

Fig.3 は Ba island が双晶となっていることを示しているとありますが、個々の island は双晶を含まない単結晶であっても、Mo(110)表面に対して二通りの成長方向があると、これらの island からの回折スポットが重ね合わさって双晶同様のパターンとなっていると考えることもできます。必ずしも双晶だけではないと思いますがいかがでしょうか。

**[著者]**

ご指摘のとおり、必ずしも双晶だけではなく Mo(110)表面上[001]Mo 方位に対して対称関係にある二通りの成長の寄与も同等と解釈されます。このことを考慮して文面を改訂致しました。